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PREPARATION AND SODIUM-AMMONIA REDUCTION OF SOME CONJUGATED ALKADIENES.

RICHARD DANIEL BRANE

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PREPARATION AND SODIUM-AMMONIA REDUCTION OF SOME CONJUGATED ALKADIENES

by

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Lieutenant, United States Naval Reserve
B.S., Duquesne University, 1958

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ABSTRACT

A series of alkadienes was prepared by the dehydration of unsaturated C_7 and C_8 alcohols. The dienes were separated by G.P.C. techniques and identified by their NMR and IR spectra. The UV data of the conjugated dienes was also recorded.

The dehydration of 4-ethyl-1-hexen-4-ol gave three dienes, 4-ethyl-1, 3-hexadiene, 4-ethyl-1,4-hexadiene and 3-ethyl-2, 4-hexadiene. The dehydration of 4-methyl-1-hexen-4-ol gave four dienes, 4-methyl-1,4-hexadiene, 2-ethyl-1,4-pentadiene, 4-methyl-1,3-hexadiene and 3-methyl-2,4-hexadiene. The dehydration of 4-octen-2-ol gave 1,3-octadiene and 2,4-octadiene in about equal amounts.

The sodium-ammonia reduction products of 2,5-dimethyl-2, 4-hexadiene, 1,3-octadiene, and 2,4-octadiene were determined. The reduction of 2,5-dimethyl-2, 4-hexadiene gave both the symmetrical and unsymmetrical olefin as reduction products. One reduction of 1,3-octadiene gave 2-octene. The other reductions of 1,3-octadiene and 2,4-octadiene gave mixtures of olefins as their monomeric products.

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1. Introduction

The Birch reduction has been demonstrated to only partially reduce organic compounds containing conjugated double bonds. This reduction using an alkaline or alkaline earth metal in liquid ammonia has been used to reduce conjugated alkadienes to alkenes.

A study of the Birch reduction of certain seven and eight carbon conjugated dienes with sodium in liquid ammonia was made with the hope of better understanding the mechanism of the reaction. Some of the alkadienes were sythesized by the dehydration of unsaturated alcohols. Reaction products were characterized by their infrared, ultraviolet, and nuclear magnetic resonance spectra. Gas chromatography was used to separate reaction components and determine their purity.

The results of the Birch reduction of some conjugated alkadienes are compared with other investigations of the reduction of conjugated dienes.

The dehydration of unsaturated alcohols with sodium hydrogen sulfate gave more complex mixtures of dienes than anticipated. Without preparative gas chromatography and nuclear magnetic resonance spectra, these dienes could not have been separated and identified.

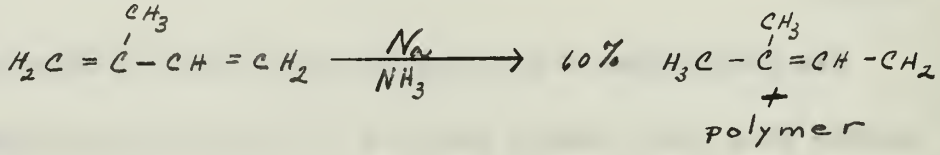
2. Historical

The reduction of aromatic compounds using the reducing medium sodium in liquid ammonia was demonstrated by Wooster[1] in 1937. The reaction has since been further investigated by Birch[2] and is commonly referred to as the Birch Reduction.

Sodium in liquid ammonia will reduce numerous classes of organic compounds such as aromatics, acetylenic and conjugated olefinic hydrocarbons, alkyl halides and unsaturated alcohols. The Birch Reduction is extensively reviewed in three relatively recent articles.[3,4,5]

Discussion of the Birch Reduction will be limited to information applicable to the reduction of conjugated alkadienes. Also two methods used for synthesis of conjugated alkadienes will be covered.

Midgley and Henne[6] first reported the reduction of alkadiene with sodium in liquid ammonia. They reduced isoprene to 2-methyl-2-butene with some polymerization.



[1]C. B. Wooster and K. L. Godfrey. J. Am. Chem. Soc., 59, 596-7 (1939).

[2]Herchel Smith. Organic Reactions in Liquid Ammonia, John Wiley and Sons, Inc., New York, N.Y., 1963, p. 244.

[3]George W. Watt. Chem. Rev., 46, 317-356 (1950).

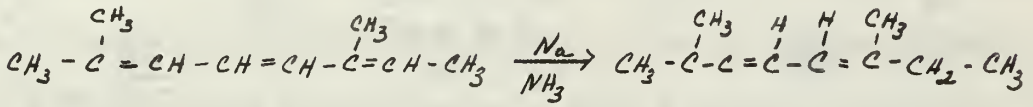
[4]A. J. Birch. Quart. Rev., 4, 69-93 (1950).

[5]A. J. Birch and Herchel Smith. Quart. Rev., 12, 17-33 (1958).

[6]T. Midgley and A. Henne, J. Am. Chem. Soc., 51, 1293 (1929).

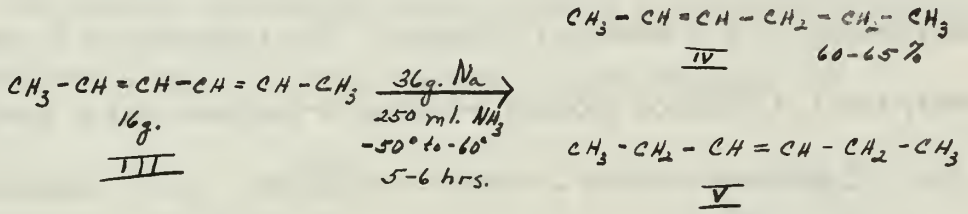
Hinkel and Bretshneider[7] investigated the reduction of butadiene and reported reduction products of 2-butene and octadiene.

The reduction of the natural product alkoocimene (I) to 2,6-dimethyl-3, 5-octadiene (II) was reported by Dupont, et al.[8]



I II

Levina, et al.,[9,10] reported in 1950 the reduction of two symmetrical dienes with sodium in liquid ammonia. The reduction of 2,4-hexadiene (III) yields a mixture of 2-hexene (IV) and 3-hexene (V). Both hexenes contained about 30 per cent cis- and 70 per cent trans- configurations as determined from their Raman spectra.



III IV V

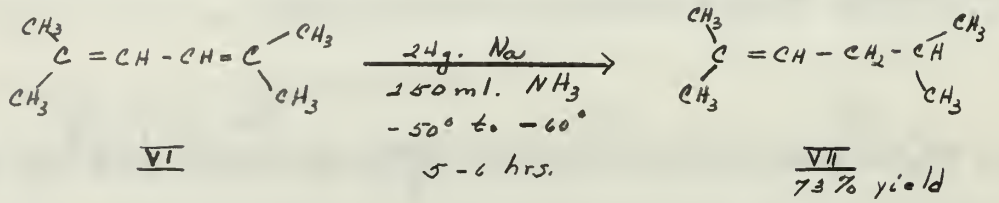
[7]W. Huckel and H. Bretshneider. Annalen, 540, 159 (1939). Chem. Abstr. 34, 96[2] (1940).

[8]G. Dupont, R. Dulou, V. Desreux, and R. Picout. Bull. Soc. Chem. (France), 5, 322-36 (1938).

[9]R. Ya. Levina, V. R. Skvarchenko, V. M. Tatevski and E. G. Treshchova. J. Gen. Chem. (U.S.S.R.), 20, 684 (1950).

[10]R. Ya. Levina, V. R. Skvarchenko, E. A. Viktorova, V. M. Tatevski and E. G. Treshchova. J. Gen. Chem. (U.S.S.R.), 20, 690 (1950).

In the reduction of 2,5-dimethyl-hexadiene (VI) only the unsymmetrical olefin 2,5-dimethyl-2-hexene (VII) was found.



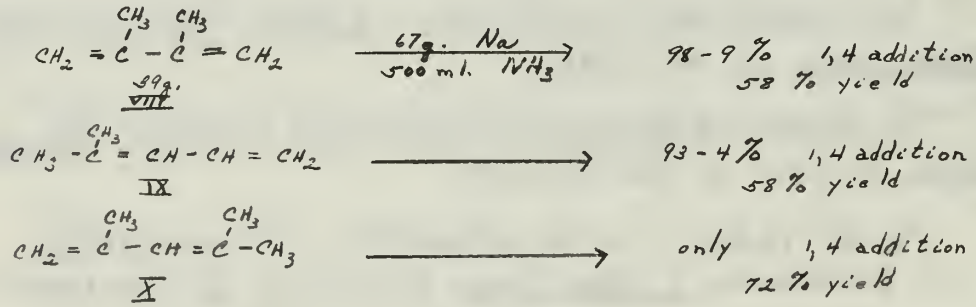
VI → VII, 73% yield

Levina comments that their

> "research refutes the established notion that hydrogen is added to a system of conjugated double bonds (the instant it is formed) at the 1,4 position, independent of the structure of the hydrocarbon."

However, Levina et. al.[11] in 1953 reported three more conjugated dienes: 2,3-dimethylbutadiene (VIII) 2-methyl-2,4-pentadiene (IX) and 2,4-dimethyl-1,3-pentadiene (X) which gave mostly 1,4 addition.

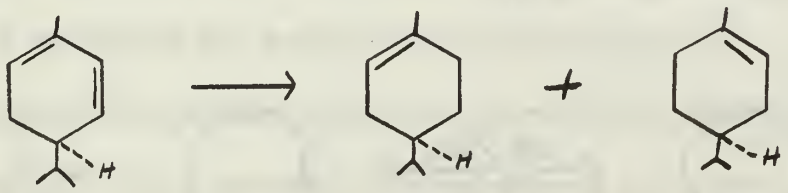
The reduction of VIII gave mostly 2,3-dimethyl-2-butene and a small amount of 2,3-dimethyl-3-butene. The reduction of IX also gave mostly the 1,4 addition product 2-methyl-3-pentene with a small amount of the 1,2 addition product 2-methyl-3-pentene. In the reduction of X, only the 1,4 addition product 2,4-dimethyl-2-pentene was found, no contaminent of 1,2 addition being found in the Raman spectra.



[11] R. Ya. Levina, V. R. Skvarchenko, V. N. Kostin, E. G. Treshchova and A. S. Okunevich. Sbornik Statei Obshchei Khim., Akad. Nauk, S.S.S.R., 1, 355 (1953). Chem. Abstr., 49, 829 (1955).

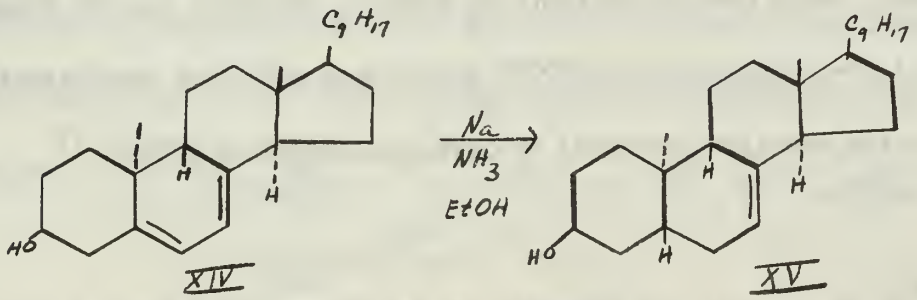
The reduction of conjugated alkadienes all show predominately 1,4-addition except for 2,5-dimethyl-2,4-hexadiene (VI) and 2,4-hexadiene (III), when reduced with sodium in liquid ammonia.

In the reduction of cyclic 1,3-dienes, 1,2-addition seems to predominate[12] with the exception of steroids of the lanostane family. Some examples of the Birch reduction of cyclic 1,3-dienes follow. (-)- α-Phellandrene (XI) is reduced by Birch Reduction to 60 per cent (-)-1-menthene (XII) and 40 per cent (+)-1-menthene (XIII).[13]



XI XII XIII

The steriod Lumisterol (XIV) is reduced to mostly 5β-lumista-7, 22-diene-3β-ol; (XV) using sodium in liquid ammonia.[14]



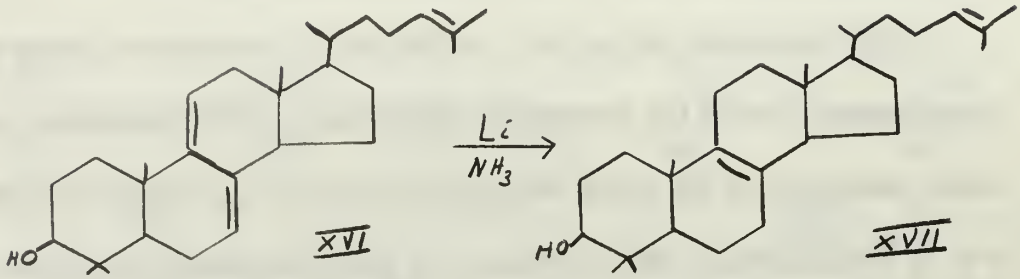
XIV XV

[12]Herchel Smith. Organic Reactions in Liquid Ammonia, John Wiley and Sons, Inc., New York, N.Y., 1963, p. 224.

[13]A. J. Birch, unpublished work cited by H. Smith, Organic Reactions in Liquid Ammonia. John Wiley and Sons, Inc., New York, N.Y. 1963, p. 224.

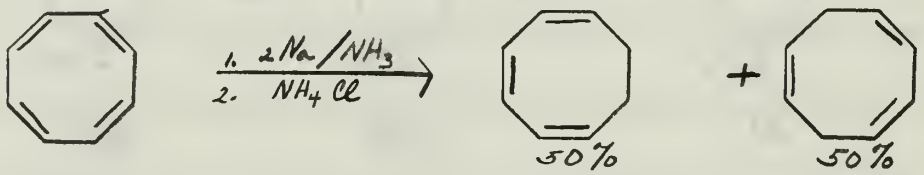
[14]J. Castells, G. A. Fletcher, E. H. R. Jones, J. D. Meakins and R. Swindell. J. Chem. Soc., 2627 (1960).

Lanosta-7,9(11),24-triene-3β,21-diol (XVI) gives only one product XVII, a 1,4 addition to the conjugated diene.[15]



XVI XVII

Cyclo-octatetraene (XVIII) upon treatment with two equivalents of sodium in liquid ammonia gave 1,3,5-cycloctatriene (XIX) and 1,3,6-cycloctatriene (XX).[16]



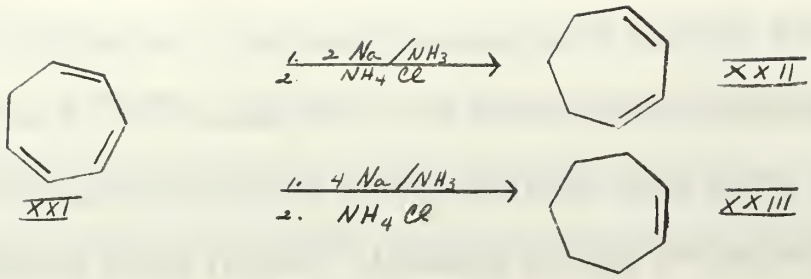
XVIII XIX XX

The reduction of 1,3,5-cycloheptatriene (XXI) has also been reported. With two equivalents of sodium, reaction can be stopped at the 1,3-cycloheptadiene (XXII) stage; and with four equivalents of sodium the reaction proceeds to give cycloheptene (XXIII).[17]

[15] S. Brewis, T. G. Halsall, G. C. Sayer. J. Chem. Soc., 2763 (1962).

[16] A. C. Cope and F. A. Hochstein. J. Am. Chem. Soc., 72, 2515 (1950).

[17] A. P. terBorg and A. F. Bickel. Rec. Trav. Chim., 80, 1229 (1961).

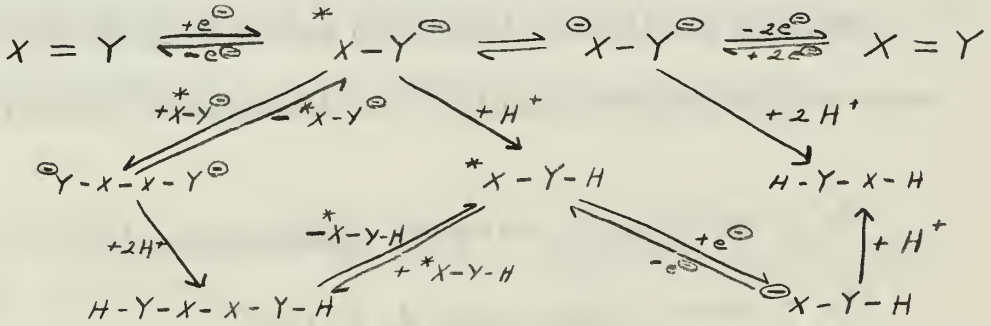


XXI XXII XXIII

The only mono-olefinic compounds which have been reduced with sodium in liquid ammonia have had the double bond in the terminal position. This reduction will not go unless methanol was present as a protonating agent. As an example of this reduction, 1-hexene was reduced to hexane by sodium and methanol in liquid ammonia.[18]

The Michaelis-Shubert theory for reductions by alkali or alkaline earth metals in liquid ammonia or other solvent has almost general acceptance.[19]

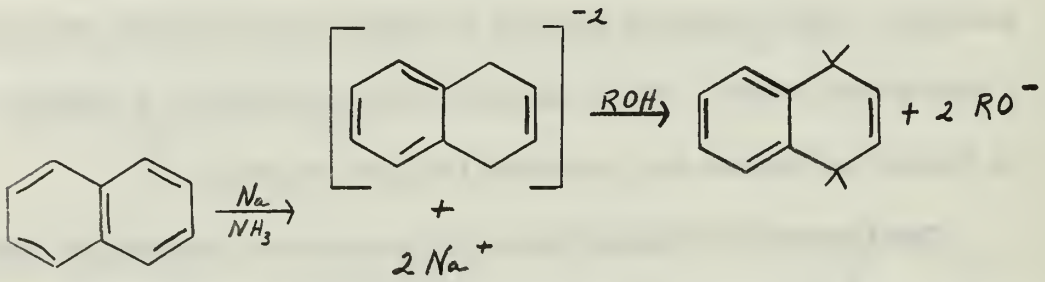
The biggest defect of the theory is that it does not consider the effect that actions of the different metals have in determining the products in the reduction. The Michaelis-Shuberts theory postulates both anion and anion-radica in the course of reduction and is summarized below.



[18]H. Greenfield, R. A. Friedel and M. Orchin. J. Am. Chem. Soc., 76, 1258, (1954).

[19]Herchel Smith. Organic Reactions in Liquid Ammonia, John Wiley and Sons, Inc., New York, N.Y., 1963, p. 154.

In the reaction of polynuclear compounds, the reduction sometimes can be experimentally carried out in two steps.[20,21] First, the initial addition of the metal electrons to form an ionized salt, then the addition of a proton source such as methanol. There is ample evidence the first step is reversible. If the reaction is carried out in one step, the same reaction products occur. The reduction[21] of naphthalene can be carried out in one or two steps.



In the Birch Reduction of conjugated alkadienes, a two-step process cannot be applied since the liquid ammonia acts as a proton donor.[6,7,9,10,11] Differences in reaction products due to addition of alcohol as a proton source have not been reported in the sodium-liquid ammonia reduction of alkadienes.

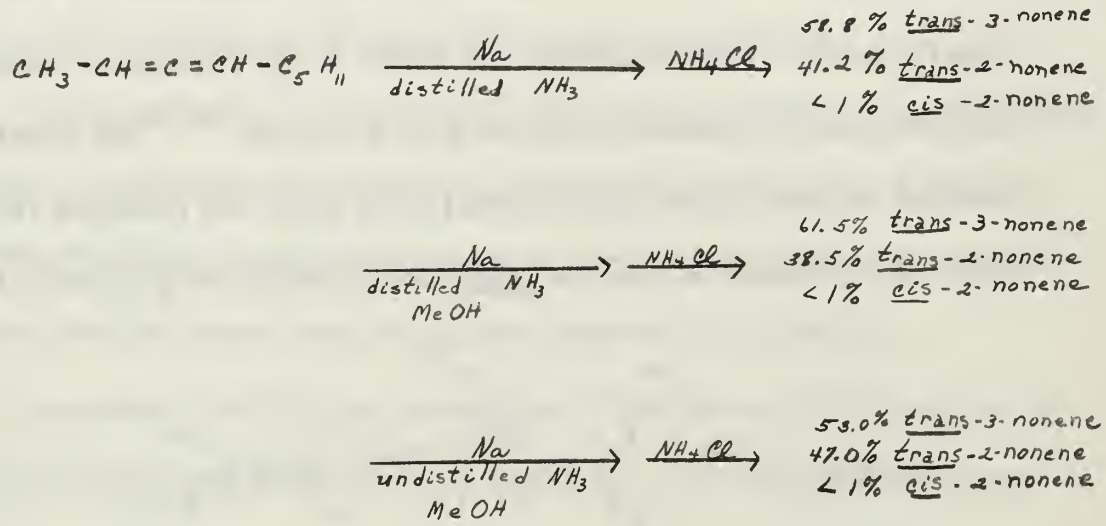
Methanol reacts very slowly with sodium in liquid ammonia but reacts with anions very rapidly.[21] de Montellano[22] found that by

[20]A. J. Birch and D. Nasipuri. Tetrahedron, 148-53 (1959).

[21]A. J. Birch. Quart. Rev., 4, 69 (1950).

[22]Bernard R. Ortiz de Montellano, PhD Dissertation, University of Texas, Austin, Texas (1965).

adding methanol as a proton source to a sodium in liquid ammonia solution, a different distribution of products in the reduction of 2,3-nonadiene (XXIV) resulted. He also found that the use of undistilled commercial ammonia containing detectable amounts of colloidal iron in the Birch Reduction of 2,3-nonadiene also affected the distribution of reactants.



Colloidal iron is undesirable because traces of iron salts catalyze the reaction between sodium and liquid ammonia to form sodium amide.[23]

Krapcho and Bothner-By[24] found that ammonium chloride and water react rapidly with alkali metals dissolved in liquid ammonia.

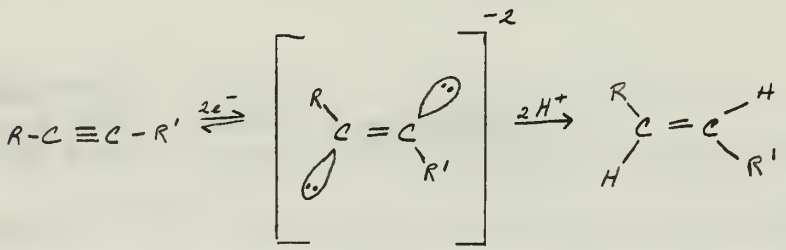
[23]T. H. Vaughn, R. R. Vogt and J. A. Niewland. J. Am. Chem. Soc., 56, 2120 (1934).

[24]A. P. Krapcho and A. A. Bothner-By. J. Am. Chem. Soc., 81, 3658-66 (1959).

The acid, ammonium chloride, has been used to quench the metal-ammonia reduction since it both removes the sodium dissolved in the ammonia and reacts with any strong base present, e.g., sodium amide.[3]

The reduction of acylic acelytenes is always stereospecific and leads to the formation of trans-olefins.[25]

The mechanism for the reduction of acylic acetylenes, which is usually given, is two electrons are added to the triple bond either successively or simultaneously to give a dianion.[26,3] The negatively charged orbitals in the dianion repel each other and therefore the molecule is forced to take the trans-configuration on protonolysis.



In the reduction of 2,3-nonadiene,[22] a similar mechanism has been postulated for the formation of trans-2-nonene and trans-3-nonene. However, in the reduction of cyclic acelytenes and allenes, the results are much more ambiguous.

[25] K. N. Campbell and L. T. Eby. J. Am. Chem. Soc., 63, 216 (1941).

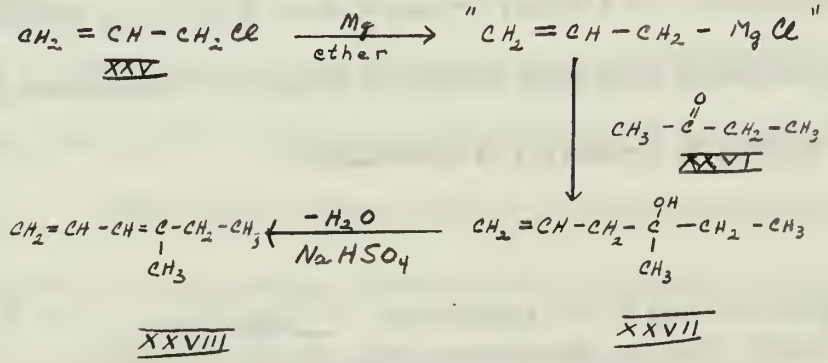
[26] K. W. Greenlee and W. C. Fernelius. J. Am. Chem. Soc., 64, 2505 (1942).

The stereochemistry of the products of the Birch Reduction of conjugated aliphatic dienes has only been reported for 2,4-hexadiene. The reduction of 2,4-hexadienes gave 2-hexene and 3-hexene, both products with about 70 per cent trans- and 30 per cent cis-configurations.[9]

There are many methods for preparing conjugated dienes but only three papers immediately applicable to the preparation used in this research will be covered. Egloff[27] gives many references for papers which have determined the physical constants of dienes.

Milas and Alevy[28] report the preparation of 4-methyl-1,3-hexadiene (XXVIII) from the starting organics, allyl chloride (XXV) and 2-butanone (XXVI). They first made the Grignard of allyl chloride and then treated it with 2-butanone to form 4-methyl-1-hexene-3-ol (XXVIII).

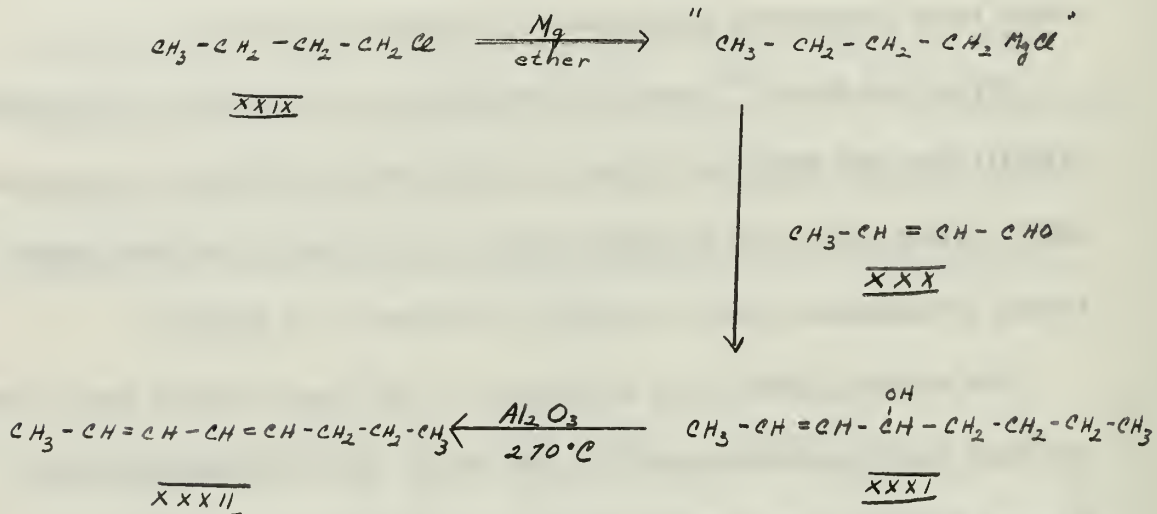
The alcohol (XXVII) was dehydrated to the diene (XXVIII) and an 88 per cent yield was determined for this step. (The dehydration of the alcohol (XXVII) in our research only gave a small amount of the diene (XXVII).)



[27]Gustav Egloff. Physical Constants of Hydrocarbons, Vol V, Reinhold Publishing Corporation, New York, N.Y., 1053, pp. 402-453.

[28]N. A. Milas and A. McAlevy. J. Am. Chem. Soc., 57, 580 (1935).

Karasev and Khabarova[29] reported the preparation of 2,4-octadiene (XXXII). The Grignard of butyl chloride (XXIX) was prepared and treated with crotonaldehyde (XXX) to form 2-octene-4-ol (XXI). The alcohol (XXI) was dehydrated to 2,4-octadiene (XXXII). The yield in the dehydration step was not reported.



The dehydration[30] of 4-ethyl-1-hexen-4-ol (XXXIII) by heating with sulfuric or oxalic acid gave chiefly 4-ethyl-1,3-hexadiene (XXXIV) with a small amount of 4-ethyl-1,4-hexadiene.

[29]K. I. Karasev and A. V. Khabarova. J. Gen Chem. (U.S.S.R.), 10, 1641-6 (1940), Foreign Petroleum Tech. 9, 42-52 (1941).

[30]Ya. M. Slobodin. J. Gen. Chem. (U.S.S.R.), 8, 241-53 (in English 254) (1938). Chem. Abstr., 32, 5371[9] (1938).

3. Experimental Part I

Preparation of some Seven- and Eight-Carbon Alkadienes.

Seven- and eight-carbon alkadienes were prepared by dehydrating unsaturated alcohols. The alcohols were prepared by either (1) the Grignard reaction of allyl chloride with a saturated ketone or (2) the Grignard reaction of butyl chloride with crotonaldehyde. Activated alumina at 270°C, $NaHSO_4$ or $KHSO_4$ were used to dehydrate the unsaturated alcohols to mixtures of dienes.

Dienes were separated on a gas chromatograph, Aerograph Autoprep, Model A-700 using a thermal conductivity detector. A 20 foot by 3/8 inch 30 per cent SE-30 on 45/60 mesh Chrombsorb W column was used at a flow rate of 200 cc/minute. Analytical chromatography was performed on an Aerograph Hy-Fy Model 600 using a flame ionization detector. A 5 foot by 1/8 inch 5 per cent SE-30 on 60/80 mesh Chrombsorb W column and a 6 foot by 1/8 inch 5 per cent carborwax on 30/60 mesh teflon column were used at a flow rate of about 20 cc/minute.

Infrared spectra were recorded on a Perkin-Elmer Infrared Spectrograph Model 337. All liquids were done neat between sodium chloride disks. NMR spectra (given in ppm tau) were recorded as given in Appendix II. Ultraviolet spectra were recorded on a Beckman DK1-A spectrophotometer using 100 per cent ethanol as solvent.

[31]M. S. Kharasch and C. F. Fuchs. J. Org. Chem., 9, 359 (1944).

Preparation of 4-Ethyl-1-Hexene-4-ol (XXIII)

The Grignard of allyl chloride was prepared by a method similar to that used by Kharasch and Fuchs.[31] Into a 2 liter three necked round bottom flask equipped with power stirrer, reflux condenser and nitrogen atmosphere was placed 40 g. (1.7 moles) of magnesium turnings in 200 ml. of ethyl ether. Allyl chloride (133 ml., 1.56 moles) in 200 ml. ether was added to the reaction mixture of 0°C. About 40 drops of allyl chloride was initially added to the reaction mixture.

After the reaction mixture had become cloudy, indicating the reaction had been initiated, the remainder of the allyl chloride was added dropwise over a four hour period. About 150 ml. of ether was added during the reaction to permit the stirring of the white slurry. The reaction mixture was stirred three more hours, then the reaction flask was cooled in a -5° salt-ice bath and 150 ml. (1.42 moles) of 3-pentanone was added over a 45 minute period. The reaction mixture was allowed to stir over night and then poured into 1000 ml. of ice to react any unused allyl chloride Grignard present. The ether layer was separated from the white sludge-water layer. The sludge-water layer was washed with 100 ml. of 15 per cent sulfuric acid. The sludge-water was extracted with ether and added to the ether solution collected. The ether was distilled leaving the reaction product, 4-ethyl-1-hexene-4-ol. The alcohol was vacuum distilled (26°/.08-.09 mm, Lit[32] b.p. 48°/12 mm). The alcohol contained less than 5 per cent 3-pentanone as determined by G.P.C. analysis. The retention time

for the alcohol on a five foot "SE-30" column was 4.6 minutes at 85°C.

The IR, (Spectrum #1 and Spectrum #2, Appendix I) had identifying bands at 3440, 1150 (-OH) and 3070, 1820, 1640 (CH_2 = CH-) cm^{-1}. The small peak at 1690 corresponds to a very strong absorption in 3-pentanone.

Dehydration of 4-Ethyl-1-Hexen-4-ol

4-Ethyl-1-hexen-4-ol (35 ml., 2.30 mole) in 150 ml. of benzene was dehydrated with .5 gm $NaHSO_4$. Water was removed by distilling a benzene-water azeotrope from the system, removing the water that separates when benzene cools and then returning the benzene to the system. When no more water was being removed from the system, the reaction mixture was washed with water to remove the $NaHSO_4$. G.P.C. analysis of the dehydration product on the 5 ft. "SE-30" column showed four peaks besides the solvent benzene with retention times of 2.1, 2.6, 3.0 and 4.6 minutes at 85°C. After the benzene was distilled, the lowest boiling component of the dehydration of 4-ethyl-1-hexene-4-ol (XXIII) was separated on a spinning band distillation column and identified as 4-ethyl-1,4-hexadiene with the following properties. N.M.R. (Spectrum #1, Appendix II) multiplets centered at 4.58 and 7.21 ppm, quartet centered at 7.96 ppm, doublet centered at 8.41 ppm, and triplet centered at 9.03 ppm in the ratio 4:2:2:3:3. IR (Spectrum #3

[32]H. Gutmann, O. Isler, G. Ryser, P. Zeller and B. Pellmont, Helv. Chem. Acta, 42, 719-28, (1959) Chem. Abstr., 53, 5371[9](1959).

and Spectrum #4; Appendix I): 3070, 3000, 1825, 1640, 992, 908, 822 cm^{-1}. No. U. V. λ_{max} above 210 mμ . Lit b. p: 121-123°, n_D^{20} 1.44346[33].

The four components from the benzene solution were separated on the Autoprep using the 20 ft. "SE-30" column with auto injection of 0.21 ml. directly onto the column. Temperature programming was employed with temperature at start of cycle at 100°C. A cooling period of six minutes was used between cycles. The first three components were separated during the heating cycle and the fourth component, found to be the starting material 4-ethyl-1-hexen-4-ol, was recovered during the next cycle. The first component to come through the column was identical to the 4-ethyl-1,4-hexadiene separated by the spinning band distillation column.

The second component separated on the Autoprep was the conjugated diene, 4-ethyl-1,3-hexadiene with following properties. NMR Spectrum #2, Appendix II): multiplets centered at 3.62, 4.30, 5.00 and 7.93 ppm, overlapping triplets centered at 8.97 and 9.00 ppm in the ratio 1:1:2:4:6. IR (Spectrum #5 and Spectrum #6, Appendix I): 3070, 3030, 1790, 1670, 1640, 984, 894, 804, 660 cm^{-1}. U.V.: λ_{max} (EtOH) 235.5 mμ, ϵ_{max} 18,300. Lit. b.p. 123-124° n_D^{20} 1,44897[33].

The third component was identified as 4-ethyl-2,4-hexadiene with the following physical constants. NMR (Spectrum #3, Appendix II):

[33] Beilsteins Handbuch Der Organischen Chemie, 4. Aufl. 3. Erg.-Werk, Bd. I/1/ (1958), page 1009.

multiplets centered at 4.25 ppm, 7.88 ppm, 8.23 ppm and 9.00 ppm in the ratio 3:2:6:3. IR (Spectrum #7 and Spectrum #8, Appendix I): 3020, 1860, 961, 926, 780 cm^{-1}. U. V.: λ_{max} (EtOH) 232.0 mμ , ϵ_{max} 22,400.

The per cent of products from the dehydration of 4-ethyl-1-hexen-4-ol was determined by vapor phase chromatography to be 60.0 per cent 4-ethyl-1,4-hexadiene, 4.7 per cent 4-ethyl-1,3-hexadiene, 15.8 per cent 4-ethyl-2,4-hexadiene and 19.5 per cent starting material.

Preparation of 4-Methyl-1-hexen-4-ol[28,31]

Allyl magnesium Grignard was prepared from 1.7 moles of magnesium turnings and 1.56 moles of allyl chloride in the same manner as in the preparation of 4-ethyl-1-hexene-4-ol. To the allyl magnesium Grignard cooled in a -5^{o} salt-ice bath was added 125 ml. (1.39 moles) of 2-butanone dropwise over a half hour period while maintaining gentle reflux. The reaction mixture was stirred one more hour, then poured onto about 1000 ml. of ice to remove any unreacted Grignard.

The ether and water solutions were washed with 200 ml. of 15 per cent H_2SO_4 and the water solution extracted with ether. The ether solutions were collected together, washed with water and the ether distilled. The higher boiling reaction products were then distilled yielding 102g. (0.803 moles) of 4-methyl-1-hexene-4-ol, 61.8 per cent of theoretical yield. The alcohol distilled over at 52-56^{o}C/20 mm., lit[28] b.p. 138-139^{o}C, 69-71^{o}C/60 mm. The alcohol contained less than 5 per cent 3-pentanone as determined by G.P.C. analysis. The

retention time of 4-methyl-1-hexene-4-ol on a 5 foot "SE-30" column was 2.8 min/85°C. The IR (Spectrum #9 and Spectrum #10) had identifying bands at 3490, 1145 (-OH) and 3080, 1820, 1640, 992, 910 cm^{-1} (CH_2 = CH-). The small peak at 1700 cm^{-1} in the IR spectrum corresponds to a strong absorption band in 2-butanone.

Dehydration of 4-Methyl-1-hexen-4-ol

4-Methyl-1-hexen-4-ol (25g., 0.20 moles) was dehydrated by distilling from 10g. $NaHSO_4$. A gas phase chromatogram of the dehydration mixture showed eight peaks using the 20 foot "SE-30" column. The retention times for the eight peaks at 100°C were (1) 14.2 min., (2) 15.6 min., (3) 16.3 min., (4) 19.2 min., (6) 25.0 min., (7) 27.2 min., and (8) 38.0 min.

The components of the dehydration product of 4-methyl-1-hexen-4-ol were separated into five fractions using the Autoprep with injections of 0.1 ml. of the dehydration product per collection cycle. The first and fifth fraction collected by the Autoprep contained products corresponding to one peak on the chromatograph. The other three fractions each contained products corresponding to two peaks. The separation and analysis of the reaction products of 4-methyl-1-hexene-4-ol is summarized in Table One.

TABLE ONE

DEHYDRATION PRODUCTS OF 4-METHYL-1-HEXEN-4-OL

Fraction Separated on Autoprep	Order of Elution from "SE-30" column	Assigned Structure	Per cent of Dehydration Product	Literature[29] Boiling Point, °C
I	1	$CH_2=CH-CH_2-\overset{CH_2}{\overset{\|\|}{C}}-CH_2-CH_3$	10%	89.5-90.0/750mm.
II	2 and 3	$CH_2=CH-CH_2-\overset{CH_3}{\overset{\|}{C}}=CH-CH_3$ <u>cis</u> and <u>trans</u>	39%	92.1-92.3/752mm.
III	4 and 5	$CH_2=CH-CH=\overset{CH_3}{\overset{\|}{C}}-CH-CH_3$ <u>cis</u> and <u>trans</u>	26%	101.8-102.0/754mm.
IV	6 and 7	$CH_3-CH=CH-\overset{CH_3}{\overset{\|}{C}}=CH-CH_3$	12%	111.8-112.3/744mm.
V	8	$CH_2=CH-CH_2-\overset{CH_3}{\overset{\|}{\underset{OH}{\underset{\|}{C}}}}-CH_2-CH_3$	12%	138-139°

The first component eluted by the Autoprep was determined to be 2-ethyl-1,4-pentadiene. The IR spectrum (Spectrum #11 and #12, Appendix I) is very distinctive with absorptions accountable to terminal olefinic bands at 3080, 1820, 1770, 1635 (two overlapping peaks), 988, 908 and 884 cm^{-1}. The sample sent for NMR analysis partially rearranged to 4-methyl-1,4-hexadiene. From the NMR (Spectrum #4, Appendix II) of the mixture of 4-methyl-1,4-hexadiene and 2-ethyl-1, 4-pentadiene and the NMR (Spectrum #5, Appendix II) of 4-methyl-1, 4-hexadiene, the following NMR values were determined for 2-ethyl—1, 4-pentadiene; a singlet at 5.22 ppm, doublet centered at 7.25 ppm, quartet centered at 7.95 ppm and triplet centered at 8.99 ppm. The olefinic proton absorptions at about 4.5 ppm of 2-ethyl-1,4-pentadiene could not be determined from the NMR spectrum of the mixture. Lit[34] NMR values were reported as a triplet at 9.00 ppm, quarter at 7.98 ppm, doublet at 7.27 ppm, singlet at 5.27 ppm and multiplets at 4.97, 4.95 and 4.30 ppm. There was no λ_{max} in the U.V. above 210 mμ. The overlap of the two peaks in the gas chromatolgraph was too great to estimate a ratio of isomers.

The second fraction (two components) separated on the Autoprep was determined to be a mixture of the isomers of 4-methyl-1,4-hexadiene with following properties. U.V.: no λ_{max} above 210 mμ. IR (Spectrum #13 and Spectrum #14, Appendix I): 3080, 3020, 1810, 1630, 987, 903, 820 and 641 cm^{-1}. NMR: (Spectrum #5, Appendix II): multiplets

[34]N. F. Cywinski. J. Org. Chem, 30, 361-4 (1965).

centered at 4.12 ppm and 5.00 ppm, doublet centered at 7.30 ppm, and a multiplet centered at 8.40 ppm, in the ratio 1:1:1:3. Lit[34] NMR values for 4-methyl-1-cis-4-hexadiene: multiplets at 4.35, 4.75, 5.00 and 5.02 ppm, doublet at 7.28 ppm and a singlet-doublet at 8.38 ppm. Lit[34] NMR values for 4-methyl-1-trans-4-hexadiene: multiplets at 4.33, 4.79, 4.98 and 5.00 ppm, doublet at 7.32 ppm and a singlet-doublet at 8.45 ppm.

The third fraction, containing the components corresponding to the fourth and fifth peaks on the chromatogram, was determined to consist of two isomers of 4-methyl-1,3-hexadiene with the following properties. U.V.: λ_{max} (EtOH) 235.0 mμ, ϵ_{max} 2.62×10^4. IR (Spectrum #15 and Spectrum #16, Appendix I): 2880, 1795, 1700 and 1600 (doublet), 982, 894 and 655 cm^{-1}. NMR (Spectrum #6, Appendix II): multiplet centered at 3.36 ppm, doublet centered at 4.16 ppm, two overlapping doublets centered at 4.92 ppm, quartet centered at 7.90 ppm, singlet at 8.22 ppm, and two overlapping triplets with center peaks at 8.8 and 8.9 ppm in the ratio 1:1:2:2:3:3. The area of the gas chromatograph peaks indicate a ratio of isomers of 1:1.4, however, no attempt was made to determine which peak corresponded to the cis or trans- isomer.

The fourth fraction of components collected, corresponding to the sixth and seventh peaks in the chromatograph, polymerized to a colorless polymer while being stored for several weeks in a refrigerator. Analysis of the samples immediately after separation on the autoprep gave the following values. U.V.: λ_{max} (EtOH) 231.0 mμ, ϵ_{max} 2.30×10^4.

IR (Spectrum #17 and Spectrum #18, Appendix I): 3030, 1855, 1800, 1730, 1640, 1023, 964, 921, 834, 822 and 768 cm^{-1}. The sample sent for NMR analysis (Spectrum #7, Appendix II) had characteristics as follows: singlet at 2.63 ppm, multiplet centered at 4.0 ppm, doublet centered at 7.75 ppm, multiplet at 8.8 ppm and multiplets 8.3-9.3 ppm.

The NMR, U.V. and I.R. indicate the sixth and seventh peaks on the chromatographic spectrum corresponds to the isomers of 3-methyl-2, 4-hexadiene. The NMR of each isomer of 3-methyl-2,4-hexadiene should show a multiplet in the range 3.5-5.0 ppm due to the three olefinic hydrogens and two doublets and a singlet at about 8.2 ppm for the hydrogens on the three methyl groups adjacent to double bonds. The extra peaks on the NMR (Spectrum #7, Appendix II) are probably due to polymerization products of 3-methyl-2,4-hexadiene. The ratio of the areas of the peaks was 1:1.4, but no effort was made to determine which isomers of 3-methyl-2,4-hexadiene corresponded to each of the two peaks.

The last fraction collected on the Autoprep was the starting material, 4-methyl-1-hexene-4-ol. Each fraction separated on the Autoprep had better than 98 per cent separation from the other fractions as determined by analysis of their gas chromatograms.

Greater amounts of the conjugated dienes, 4-methyl-1,3-hexadiene and 3-methyl-2,4-hexadiene were separated on the Autoprep using autoinjections of 0.5 ml. for each cycle directly on the 20 foot "SE-30" column at a temperature of 105°C. The eight components were collected

in four fractions, the first fraction containing the first three components to come through the column, the second fraction containing the 4-methyl-1,3-hexadiene, the third fraction containing the 3-methyl-2,4-hexadiene and fourth fraction containing the starting material, 4-methyl-1-hexene-4-ol. The autoinjections for each cycle were made after the third fraction of components had passed out the column.

Preparation of 2-Octene-4-ol[35,29]

The general preparation of allyl magnesium Grignard is given by Kharasch and Reinmuth.[35]

Using their generalized method of preparation as a guide, the Grignard of n-butyl chloride was prepared. Magnesium turnings (54.7g., 2.25 moles) were placed into a 2 liter, three necked, round bottom flask equipped with power stirrer, reflux condenser and nitrogen atmosphere. A small amount of n-butyl chloride (11 ml.) was added to the reaction flask and stirred about a half hour until the reaction to form n-butyl magnesium Grignard had initiated. Then the remaining 200 ml. of n-butyl chloride was diluted with 700 ml. of ethyl ether and added to the solution from a dropping funnel while maintaining a gentle reflux. A total of 211 ml. (2 moles) of n-butyl chloride was used in preparing the Grignard. When the rate of refluxing was becoming too rapid, cold water was poured over the flask to slow down the rate of reflux. After addition of the n-butyl chloride the reaction mixture was stirred for two hours and allowed to sit overnight. Then the reaction mixture was cooled in a -5^{o} salt-ice bath and crotonaldehyde (94.6g.,

[35]M. S. Kharasch and O. Reinmuth, Grignard Reaction of Non-Metallic Substance, Prentice Hall, 1954.

1.35 moles) was added dropwise over one hour to the Grignard to form 2-octene-4-ol. The reaction mixture was stirred one more hour and then poured into 1000 ml. of ice.

The organic layer was poured from the top of the reaction mixture, then the rest of the mixture was extracted with ether. The organic layer and ether extracts were combined and washed with water. The ether was distilled away leaving 163 gm (1.27 moles) of 2-octene-4-ol, 94 per cent theoretical yield. The IR (Spectrum #19 and Spectrum #20, Appendix I) had identifying absorption bands at 3340 cm^{-1} (-OH) and 3020 (shoulder), 1660, 960, 725 cm^{-1} (-CH=CH-). The retention time on a five foot "SE-30" column at 110° was 5.2 minutes. Literature values for 2-hexen-4-ol are b.p. 160°C/760 mm, n_D^{25} 1.4426.[36]

Dehydration of 2-Octene-4-ol[29]

2-Octene-4-ol (119g., 0.930 moles) was dehydrated using aluminum oxide as the catalyst. The aluminum oxide used was "Activated Alumina Plain, No. 7-574" distributed by Fisher Scientific Company. The aluminum oxide was packed into a 20 inch long, 1/2 inch diameter pyrex column and heated in a furnace to the reaction temperature of 270°C. The 2-octene-4-ol was distilled through the column at pressures less than four millimeters and the reaction products collected in traps

[36] Beilsteins Handbuch Der Organischen Chemie, 4, Aufl. 3. Erg.-Werk, Bd I/2, page 1947 (1958).

cooled with liquid air.

The water layer was discarded from the dehydration products. Gas chromatographic analysis of the dehydration products showed 2-octene-4-ol had been completely dehydrated. There were two major peaks on the chromatogram with retention times of 3.1 minutes and 3.6 minutes at 85°C on the 5 foot "SE-30" column. The Autoprep was used to collect two fractions, which had retention times of 14.2 and 16.9 minutes at 115°C on the 20 foot "SE-30" column. Autoinjections of 0.15 ml. were made directly on the column for each cycle.

The first fraction collected by the Autoprep was 1,3-octadiene with following properties. U.V.: λ_{max} (EtOH) 225.0 mμ, ϵ_{max} 1.05×10^4. IR (Spectrum #21 and Spectrum #22, Appendix I): 3080, 1790, 1750, and 1700 (doublet), 996, 944, 890. NMR: (Spectrum #8, Appendix II) multiplets centered at 3.90 ppm, 4.99 ppm, 7.88 ppm, 8.62 ppm and 9.06 ppm in the ratio 3:2:2:4:3. Lit b.p. 130-1°, N_D 1.4499.[37]

The second fraction was identified as 2,4-octadiene with following characteristics. U.V.: λ_{max} (EtOH) 228.5 mμ, ϵ_{max} 1.2×10^4. IR (Spectrum #23 and Spectrum #24, Appendix I): 3010, 1690 and 1600 (doublet), 980, 942, 812 and 715 cm^{-1}. NMR (Spectrum #9, Appendix II): multiplets centered at 4.20 ppm, 7.90 ppm, two overlapping doublets centered at 8.25 ppm, multiplet centered at 8.68 ppm, and a triplet centered at 9.08 ppm in the ratio 4:2:3:2:3. Lit[23] b.p. 133.5-134.0°C/760 mm, n_D^{20} 1.4515.

[37]Kh. V. Bal'yan, Z. A. Lermin and L. A. Merkureva, Zhur. Obshchei Khim, 28, 110-16 (1958), Chem. Abstr., 52, 12746d (1958).

The dehydration product from 2-octene-4-ol contained 49 per cent 1,3-octadiene, 50 per cent 2,4-octadiene and about one per cent unidentified material as determined from the areas of the gas chromatograph peaks. The 1,3-octadiene and 2,4-octadiene separated by the Autoprep had a purity of 98 per cent or better as determined from their gas chromatograms.

4. Experimental, Part 2.

Reagents Used in the Reduction of Dienes

Commercial ammonia (U. S. Naval Supply Depot) was distilled twice for use in the reduction of the conjugated dienes. The first distillation was made from the ammonia tank, through a glass wool scrubber, into a one liter three necked round bottom flask cooled in a dry ice-acetone bath. The flask was equipped with a magnetic stirrer and three stopcocks, the first connected to the ammonia source, the second connected to a nitrogen source and the third connected to a mercury trap to prevent introduction of the outside atmosphere into the system. After sufficient liquid ammonia had been collected in the round bottom flask, a small amount of ferric chloride and metallic sodium was added to the liquid ammonia to react with any water in the liquid ammonia. The ammonia was then distilled into a second, one liter, three necked, round bottom flask equipped with a mechanical glass stirrer and a total reflux condenser cooled with a dry ice-acetone mixture. The condenser outlet was connected to a mercury trap to ensure a closed system. All glassware used in

the double distillation of ammonia was dried in an oven and purged with nitrogen before use.

2,5-Dimethyl-2,4-butadiene (Benzol Products Company No. K173) was used without further preparation. It contained 4.33 per cent impurities.[38] The major impurity was 2,5-dimethyl-1,5-hexadiene (2.93 per cent). The other impurities (1.13 per cent) contained at least nine unidentified components.

Sodium metal, Reagent A.C.S., Code 2188 (Baker and Adamson) was cut into pieces and stored under paraffin oil until used.

The conjugated dienes (1,3-octadiene, 2,4-octadiene, 4-methyl-1,3-hexadiene) were prepared and separated as reported in Section III, Experimental. They were at least 98 per cent pure as determined by G.P.C.

Reduction of 2,5-Dimethyl-2,4-hexadiene-Run One

Metallic sodium (2.0 gm, 0.088 moles) was added to 350 ml. of liquid ammonia at its boiling point. After the sodium had dissolved in the ammonia to form a dark blue solution, 1.52g. (0.0138 mole) of 2,5-dimethyl-2,4-hexadiene in 25 ml. of ether and 2.2 ml. (0.0552 moles) methanol was added to the liquid ammonia solution over a ten minute period. The reaction was stirred five more minutes, then 5g. (0.093 moles) of ammonium chloride was slowly added to quench the reaction. The dark blue color of the reaction mixture completely disappeared on addition of the ammonium chloride. The ammonia was

[38]William F. Ringk, Benzol Products Company, Cleveland, Ohio, Letter of November 30, 1966.

allowed to evaporate overnight through a mercury trap. The reaction flask was washed out with distilled water and the organic layer which separated from the water was collected.

The G.P.C. of the organic layer showed two components on the five foot "SE-30" column with retention times of 2.4 minutes and 3.3 minutes at 65°C. No ether (retention time 1 min/65°C) or starting material 2,5-Dimethyl-2,4-hexadiene (retention time 6.1 min/65°C) was found in the chromatogram.

The first component had an identical retention time as an identified sample of 2,5-dimethyl-3-hexene. The second component had an identical retention time as an identified sample of 2,5-dimethyl-2-hexene (90 per cent pure). The IR spectrum of the mixture of reduction products had only peaks corresponding to the IR spectrum of 2,5-dimethyl-2-hexene (Spectrum #25 and Spectrum #26, Appendix I), for example 1780, 1755, 1180 and 970 cm^{-1} and the IR spectrum of 2,5-dimethyl-3-hexene (Spectrum #27 and Spectrum #28, Appendix I), for example 1610, 1089, 995, 986, 852, 762 cm^{-1}.

The separation and proof of the structure of 2,5-dimethyl-2-hexene and 2,5-dimethyl-3-hexene is given on page 35.

Based on the above GPC and IR data and the expected products of reaction, it was determined the reduction of 2,5-dimethyl-2,4-hexene gave 20 per cent 2,5-dimethyl-3-hexene (Lit b.p.[27]: 103.0-103.5°C/760 mm) and 80 per cent 2,5-dimethyl-2-hexene (Lit b.p.[27]: 112.6-112.7°C/760 mm).

Reduction of 2,5-Dimethyl-2,4-hexadiene - Run Two

This reduction was carried out under the same conditions as Run One except larger quantities of reagents were used. Metallic sodium (7.6 gm, 0.33 moles) was added to 500 ml. of double distilled ammonia at its boiling point. To the dark blue solution of sodium dissolved in the liquid ammonia, 7.62 g. of 2,5-dimethyl-2,4-hexadiene (0.693 moles) in 50 ml. of ether and 11.0 ml. methanol (0.257 moles) was added over a five minute period. The reaction was stirred five more minutes and then 25 g. (0.46 moles) of ammonium chloride was slowly added to quench the reaction. The ammonia was allowed to evaporate overnight through a mercury trap. Then the reaction flask was washed out with distilled water and the oily layer which separated from the water was collected.

The organic layer from the reduction of 2,5-dimethyl-2,4-hexadiene gave two peaks (plus a small peak from the ether used as solvent) with retention times of 2.6 and 3.5 minutes at 65^{o}C on the five foot "SE-30" column. The products of the reduction were separated into two fractions on the Autoprep using manual injections of 0.25 ml. The retention time of the two components on the 20 foot "SE-30" column at 110^{o} was 28 minutes and 40 minutes.

The first fraction separated on the Autoprep was identified as 2,5-dimethyl-3-hexene with following properties: IR (Spectrum #25 and Spectrum #26, Appendix I): 3020, 1780, 1755, 1640, 1180, 1098, 972, 852, and 827 cm^{-1}. NMR (Spectrum #10, Appendix II): two

overlapping doublets centered at 4.65 ppm, a multiplet centered at 7.90 ppm and a doublet centered at 9.08 ppm in the ratio 1:1:6. Lit[27]: b.p. 103.0-103.5°C/760 mm.

The olefinic hydrogens should only be split into a doublet by the methine hydrogen in the symmetrical compound, 2,5-dimethyl-3-hexene. The presence of doublets of about equal size in the NMR at 4.65 ppm (Spectrum #10, Appendix II) indicates that about equal amounts of cis- and trans-isomers of 2,5-dimethyl-3-hexene were formed in the reaction.

The second fraction was determined to contain mostly 2,5-dimethyl-2-hexene with identifying IR bands (Spectrum #27 and Spectrum #28, Appendix I): 3040 (shoulder), 3020 (shoulder), 1670, 994, 988, 853, and 762 cm^{-1}. The NMR (Spectrum #11, Appendix II) indicates about 10 per cent of unidentified contaminents in the 2,5-dimethyl-2-hexene separated on the Autoprep. The NMR spectrum of 2,5-dimethyl-2-hexene should contain a triplet at about 4.8 ppm due to the olefinic hydrogen, a quartet at about 8.3 ppm due to the methylene hydrogens, two singlets at about 8.3 ppm due to the hydrogens on the cis- and trans-methyl groups, a multiplet at about 8.5 ppm due to the methine hydrogen and a doublet at about 9.1 ppm due to the hydrogens on the two remaining methyl groups. The recorded NMR has all the predicted peaks, plus peaks due to some impurity, e.g., peak at 8.75 ppm and a small peak between the doublet at 9.11 ppm. The amount of contaminents in 2,5-dimethyl-2-hexene was calculated using the integrated area (11.5 units) of the triplet at 4.82 ppm as a standard. This triplet was

assigned to the olefinic hydrogen in 2,5-dimethyl-2-hexene (C_8H_{16}). The integrated spectrum, if pure 2,5-dimethyl-2-hexene, should have a total integrated area of 184 units. The recorded spectrum, which has a total integrated area of 204 units, was used to calculate that the second fraction separated on the Autoprep contained 90 per cent 2,5-dimethyl-2-hexene.

One impurity possible in the second fraction is the 2.93 per cent of 2,5-dimethyl-1,5-hexadiene (Lit[27] b.p. 113-113.5) present in the starting material. This impurity has the same retention time on the five foot "SE-30" column as 2,5-dimethyl-2-hexene (Lit[27] b.p. 112.6-112.7). However, the NMR and IR spectra of the second fraction collected do not indicate the presence of this material.

The reduction of 2,5-dimethyl-2,4-hexadiene yielded 74 per cent of 2,5-dimethyl-2-hexene (90% pure) and 26 per cent of 2,5-dimethyl-3-hexene. The impurities in 2,5-dimethyl-2-hexene were not identified.

Reduction of 2,5-Dimethyl-2,4-hexadiene - Run Three

The conditions for this reaction were similar to Run Two except that methanol was added to the sodium-ammonia solution before addition of the diene. First metallic sodium (7.6 gm, 0.33 moles) and then 11.0 ml. of methanol (0.257 moles) was added to 500 ml. of double distilled ammonia at its boiling point. To the ammonia solution 7.62 g. of 2,5-dimethyl-2,4-hexadiene (0.693 moles) in 50 ml. of ether was added over a five minute period. The reaction was stirred five more minutes and then 25 g. (0.46 moles) of ammonium chloride was

added to the solution to quench the reaction. The ammonia was allowed to evaporate through a Hg. trap. The reaction flask was rinsed out with distilled water. From the water, 3.22 gm of oil separated.

A G.P.C. analysis of the oil on the five foot "SE-30" column showed three components (disregarding a very small ether peak) with retention times of 2.4, 3.3 and 6.1 min/65°C. The first component had an identical retention time as a sample of 2,5-dimethyl-3-hexene, the second component an identical retention time as a sample of 2,5-dimethyl-2-hexene, and the third component an identical retention time as the unreduced starting material, 2,5-dimethyl-2,4-hexadiene.

The IR of the reduction products had only peaks found in the IR spectrum of 2,5-dimethyl-2-hexene and 2,5-dimethyl-3-hexene.

Based on the G.P.C., IR and expected products of reaction, it was determined that the reduction of 2,5-dimethyl-2,4-hexadiene under these conditions gave 24 per cent 2,5-dimethyl-3-hexene, 74 per cent 2,5-dimethyl-2-hexene and 2 per cent unreduced diene. A yield of 42 per cent of reduced products was recovered.

Reduction of 2,5-Dimethyl-2,4-hexadiene - Run Four

The conditions for the reduction were similar to those used in Run Two except that a much longer reaction time was employed. Metallic sodium (7.6 gm, 0.33 mole) was added to 500 ml. of double distilled ammonia at its boiling point. To the dark blue solution of sodium dissolved in liquid ammonia, 7.62 g. of 2,5-dimethyl-2,4-hexadiene (0.693 moles) in 50 ml. of ether and 11.0 ml. methanol (0.257 moles) were added over a ten minute period. The reaction was stirred for 5.2

hours, then 25 gm (0.46 moles) of ammonium chloride was added to quench the reaction. The ammonia was allowed to evaporate overnight through a mercury trap. The reaction flask was washed out with distilled water and 1.70 gm of oil separated from the water. The flask was then rinsed out with ether and 1.75 gm of oil was recovered after distilling the ether.

The G.P.C. analysis of the oil on the five foot "SE-30" column showed the presence of two peaks with retention times of 2.4 and 3.3 min/65^{o}C corresponding to the retention times of 3,5-dimethyl-3-hexene and 3,5-dimethyl-2-hexene. The IR of the oil showed only absorptions present in the IR spectrum of 3,5-dimethyl-2-hexene and 3,5-dimethyl-3-hexene.

Based on the G.P.C., I.R. and expected products of reaction, it was determined that the reduction of 2,5-dimethyl-2,4-hexadiene gave 23 per cent 2,5-dimethyl-3-hexene and 77 per cent 2,5-dimethyl-2-hexene. A theoretical yield of 45 per cent of the reduction products was recovered.

Reduction of 2,5-Dimethyl-2,4-hexadiene - Run Five

The conditions for this reduction of 2,5-dimethyl-2,4-hexadiene were much different than the first four. No methanol was used as a protonating agent and the sodium-ammonia ratio was more than six times greater. Metallic sodium (25 g., 1.04 moles) was added to 250 ml. of double distilled ammonia at its boiling point. The sodium-ammonia solution was a dark bronze rather than the usual dark blue. The ammonia dripping from the condensor became blue when mixing

with the bronze solution, then gradually became bronze colored. Not all the sodium dissolved in the ammonia as evidenced by pieces of sodium in the ammonia solution and a sodium mirror which plated on the inside of the flask above the ammonia solution. After addition of the sodium, 15 g. of 2,5-dimethyl-2,4-hexadiene (0.136 moles) in 50 ml. of ether was added to the solution over a ten minute period. The reaction was stirred for five hours, then 75 g. of ammonium chloride (1.38 moles) was added slowly to the reaction. Upon addition of ammonium chloride, the solvent became colorless, however, there was metallic sodium present in the flask. The ammonia was allowed to evaporate overnight through a mercury trap. Methanol (80 ml.) and 250 ml. of ether were used to react with the metallic sodium present in the flask and to recover the reduction products. The ether layer was washed with water and the ether distilled. A total of 11.76 gm of reduction products were collected.

The G.P.C. analysis of the product on the five foot "SE-30" column showed only three peaks (plus a small ether and/or methanol peak) with retention times of 2.6, 3.5 and 7.1 min/65^{o}C. A sample containing 2,5-dimethyl-2-hexene and 2,5-dimethyl-3-hexene from the reduction of 2,5-dimethyl-2,4-hexadiene, Run Two had retention times of 2.6 and 3.5 minutes and a sample of 2,5-dimethyl-2,4-hexadiene had a retention time of 7.1 minutes under the same conditions. The IR spectrum of the reduction products only had absorptions found in the spectra of 2,5-dimethyl-2-hexene and 2,5-dimethyl-2,4-hexadiene plus some very small absorptions found in 2,5-dimethyl-3-hexene.

The products of the reduction of 2,5-dimethyl-2,4-hexadiene were determined to be eight per cent 2,5-dimethyl-3-hexene, 38 per cent 2,5-dimethyl-2-hexene and 54 per cent of the starting material. The yield of reduction products was 34 per cent with recovery of 42 per cent of starting material.

Birch Reduction of 1,3-Octadiene - Run One

1,3-Octadiene was reduced by an ammonia solution of sodium and methanol. Metallic sodium (1.0 g., 0.043 moles) and 1.1 ml. of methanol (0.026 moles) was added to 300 ml. of double distilled ammonia at its boiling point. Then 0.75 g. of 1,3-octadiene (0.0068 moles) in 25 ml. of ether was added to the dark blue ammonia solution over a five minute period. The reaction mixture was stirred five more minutes, then five grams of ammonium chloride (0.094 moles) was added to quench the reaction. The ammonia was allowed to evaporate through a mercury trap overnight. Then the reaction flask was rinsed with water and ether to recover the reduction products. The ether layer was washed with distilled water and the ether distilled. The reduction products remaining after the distillation were placed in one leg of an h-shaped pyrex tube. The distillate was cooled in liquid nitrogen and then the tube evacuated to less than 0.2 mm pressure. The tube was then sealed and the reduction products distilled over to the other leg of the "h-tube" now cooled in liquid nitrogen. Only about 25 per cent of the reduction products distilled. The reduction products not distilled were very viscous and not investigated further.

The distillate collected in the "h-tube" had overlapping peaks when analyzed on the G.P.C. using the five foot "SE-30" column. The areas of the peaks were in an approximate ratio of 1:2 with retention times of 2.8 and 3.0 minutes/85°C and 4.9 and 5.3 minutes at 65°C.

The IR (Spectrum #29 and Spectrum #30, Appendix I) had identical absorptions as a spectrum of 2-octene*, i.e., bands at 3000 (cis), 1660 (cis), 968 (trans), 930, 911, 730 and 700 (cis) cm^{-1}. Trans-3-octene also has an IR absorption at 968 cm^{-1}, however, the absorption at 968 cm^{-1} in this compound is absent in the IR of the distillate.

The NMR spectrum (Spectrum #12, Appendix II) had very high gain due to the small amount of sample analyzed. The major peaks in the spectrum are those predicted for 2-octene, for example, the doublet at 8.45 ppm corresponds to protons on the terminal methyl group split by the adjacent olefinic proton. 3-Octene, a possible product of the reduction of 1,3-octadiene, is not expected to have this absorption at 8.45 ppm.

The IR, NMR and GPC data indicate that 2-octene is the only monomeric product obtained in the reduction of 1,3-octadiene by the sodium-methanol-ammonia solution. The lit[28], b.p. for trans-2-octene is 124.94°C/760 mm and for cis-2-octene is 125.62°C/760 mm.

*Spectra of 2-octene, cis-2-octene, trans-2-octene, trans-3-octene and trans-4-octene kindly supplied by Aldrich Chem. Co., Inc., Milwaukee 10, Wisconsin.

Reduction of 1,3-Octadiene - Run Two

A solution of 1,3-octadiene containing methanol was added to a reducing solution of sodium in liquid ammonia. Metallic sodium (2.0 g., 0.086 moles) was added to 350 ml. of double distilled ammonia at its boiling point. Then 2.07 g. of 1,3-octadiene (0.0189 moles) in 25 ml. of ether and 3 ml. of methanol (0.0746 moles) was added to the dark blue sodium-ammonia solution over a five minute period. The reaction was stirred five more minutes, then five grams of ammonium chloride (0.094 moles) was added to the solution. The ammonia was allowed to evaporate overnight through a mercury trap. The reduction products were extracted with 80 ml. of ether. The ether was distilled and the remaining reduction products were placed in one leg of an h-shaped distillation tube. The reaction products were cooled with liquid nitrogen and the h-shaped tube evacuated to less than 0.2 mm and the tube sealed. The reduction products were distilled over to the other leg of the "h-tube" now cooled in liquid nitrogen. Only about 25 per cent of the reduction products distilled. The reduction products not distilled were very viscous and not investigated further.

A G.P.C. analysis of the distillate on the five foot "SE-30" column showed two overlapping peaks, the first peak much larger, with retention times of 4.6 and 4.9 min/55^{o}C respectively. On the same column, only one peak was recorded at 85^{o}C with a retention time of 2.7 minutes. On the six foot carbowax column, only one peak was recorded with a retention time of 6.5 min/85^{o}C. On the 20 foot "SE-30" column, three peaks were recorded on a temperature programmed

run, initial column temperature at 100°C, with retention times of 16.8, 19.6 and 20.8 minutes. The per cent areas of the three peaks in order of elution from the column were 4 per cent, 75 per cent and 20 per cent. The IR spectrum (Spectrum #21 and Spectrum #22) of the distilled mixture of reduction products has absorptions corresponding to cis-2-octene at 1660, 930, 911, 730 and 700 cm^{-1}. It cannot be determined if the absorption at 968 cm^{-1} is due to either of the expected products of the reduction: trans-2-octene or trans-3-octene, since both compounds have almost identical IR spectra, except trans-2-octene has the only absorption at 730 cm^{-1}. However, cis-2-octene also absorbs at 730 cm^{-1}.

The absorption at 3550 cm^{-1} is probably due to water. Two absorptions at 1710 cm^{-1} and 790 cm^{-1} have not been identified, but may be due to cis-3-octene. The spectrum of cis-3-octene available had too poor resolution to be of use.[39] Insufficient amounts of distilled reduction products were available to obtain NMR spectra.

From the reduction of 1,3-octadiene in ether and methanol added to a sodium ammonia solution cis-2-octene was identified. However, the other components in the reduction products could not be positively identified but may be trans-2-octene, cis-3-octene and/or trans-3-octene. There is no evidence of 1-octene in the reduction products. The literature[28] boiling points for expected products of the reduction of 1,3-octadiene are as follows. 1-octene: 121.27°C/76 mm, cis-3-octene: 122.7°C/760 mm, trans-3-octene: 123.29°C/760 mm, trans-2-octene: 124.94°C/760 mm and cis-2-octene: 125.62°C/760mm.

Reduction of 2,4-Octadiene

2,4-Octadiene in methanol and ether was reduced by a sodium-ammonia solution. Metallic sodium (1.75 g., 0.76 moles) was added to 300 ml. of double distilled ammonia at its boiling point. Then 1.78 g. of 2,4-octadiene (0.0160 moles) in 25 ml. of ether and three ml. of methanol (0.0745 moles) was added to the dark blue solution over a 15 minute period. The reaction was stirred five more minutes and then five grams of ammonium chloride (0.094 moles) was added to quench the reaction. The ammonia was allowed to evaporate through a mercury trap overnight. Then the reaction flask was rinsed with water and ether to recover the reduction products. The ether layer was washed with distilled water and distilled. The remaining products were placed in one leg of an "h-tube". The distillate was cooled in liquid air and the tube evacuated to less than 0.2 mm pressure. The tube was then sealed and the contents distilled over to the other leg of the "h-tube" cooled in liquid air. About 50 per cent of the reduction products distilled. The reduction products not distilled were very viscous and not investigated further.

Gas phase chromatography of the distillate on the five foot "SE-30" column gave only one peak with retention times of 2.9 min/85^{o}C and 4.5 min/65^{o}C. Using the six foot "carbowax" column at 85^{o}, only one peak was recorded with retention time of 6.3 minutes, however, by diluting the distillate with carbon tetrachloride and lowering the temperature to 65^{o}C, two almost completely separated peaks were recorded with retention times of 7.7 and 9.8 minutes. The area of

the peaks in order of elution were 15 per cent and 85 per cent.

The IR (Spectrum #33 and Spectrum #34, Appendix I) of the distillate had absorptions which probably correspond to olefinic reduction products at 3000 (shoulder), 2990, 1710, 964 and 782 cm^{-1}. The peak at 3350 cm^{-1} may be due to water present in the reduction products. The presence of cis-2-octene is not indicated by the IR spectra since absorption bands of cis-2-octene at 1660 and 911 cm^{-1} are absent. The peak at 782 cm^{-1} may be due to cis-3-octene or cis-4-octene, however, no reference spectra with sufficient resolution were available. The peak at 964 cm^{-1} is almost identical in reference spectra of trans-2-octene, trans-3-octene or trans-4-octene.

The NMR (Spectrum #13, Appendix II) of the distillate does not show a doublet at 8.47 ppm found in the spectrum of 2-octene. However, the NMR spectrum, which had a multiplet at 4.6 ppm corresponding to olefinic hydrogens, a multiplet at 8.0 ppm corresponding to hydrogen on a methylene group adjacent to an olefinic band, a multiplet at 9.7 ppm corresponding to hydrogens on a methylene group not adjacent to an olefinic band and a triplet at 9.1 ppm corresponding to methyl groups, can be attributed to 3-octene and/or 4-octene.

The reduction of 2,4-octadiene in ether and methanol by a sodium ammonia solution gave monomeric products which may be 3-octene and/or 4-octene. No 2-octene was found as a reduction product. The lit[27] boiling points for the olefinic products which may be present from the reduction of 2,4-octadiene are cis-3-octene; 122.7°C/760 mm, trans-

3-octene: 123.29°C/760 mm, cis-4-octene: 122.54°C/760 mm, and trans-4-octene: 122.10°C/760 mm.

A second sample of 2,4-octadiene was reduced with a sodium-methanol-ammonia solution. Some olefinic products were obtained but were not identified.

Reduction of 4-Methyl-1,3-hexadiene

4-Methyl-1,3-hexadiene (1.3 g., 0.014 moles) in 25 ml. of ether and 2.1 ml. of methanol (0.052 moles) was added to a solution of sodium (1.24 g., 0.054 moles) in 350 ml. of ammonia. The diene was added over a five minute period and the reaction stirred five more minutes before adding five grams of ammonium chloride (0.094 moles) to quench the reaction.

Most of the reaction product was lost in the work-up but the following results may be of use if the experiment is repeated. The IR of the reduction products had absorptions at 3020 (shoulder), 1960, 1740, 1710, 1660, 970, 912 and 810 cm^{-1} which may be due to olefinic compounds in the reduction products. A gas phase chromatogram of the reduction products gave peaks at 3.6 and 7.1 min/65°C using the five foot "SE-30" column. The retention time for the two isomers of the starting material is 2.45 and 2.60 minutes at 65°C on the same column. Insufficient data was collected to determine the reduction products of 4-methyl-1,3-hexadiene.

5. Discussion

There have been less than ten reductions of alkadienes by sodium-ammonia solutions reported in the literature. This is an indication of the great difficulty in preparing and identifying pure conjugated dienes. The alkadienes made in this research were separated on gas chromatographic columns and could not have been easily separated by other techniques available. Without NMR analysis positive identification of many of the dienes could not have been made. The IR spectra, although different for each diene, were in most cases not sufficient to identify an unknown diene. The U.V. gave a positive indication of conjugated dienes which always had a λ_{max} above 210 mμ.

Each diene had a structure which could be completely identified by its NMR spectrum. The approximate chemical shifts and characteristic splitting of the protons found in the NMR spectra of the dienes are summarized in Table II. Methyl, methylene, and methine hydrogens each have a pair of characteristic shifts, one shift when on a group non-adjacent to a double bond and a second shift at a lower ppm (tau) when on a group adjacent to a double bond. The methylene group had a third characteristic shift at a much lower ppm when directly between the two olefinic bonds in 1,4-dienes. In most cases the methyl, methylene, and methine hydrogen absorptions were completely separated in the NMR spectrum. The proton groups can also be identified by their characteristic splitting. The olefinic hydrogens absorptions occur in the 3.0-5.0 ppm range with the terminal olefinic hydrogens absorbing

TABLE II

Approximate Chemical Shifts of Protons

Proton Group	Structure	Approximate* Shift	Characteristic Splitting
Methyl	CH_3-CH_2-	9.1	triplet
	$CH_3-CH(CH_3)-$	9.1	doublet
	$CH_3-C(CH_3)-$	9.1	doublet
	$CH_3-CH=$	8.3	doublet
	$CH_3-C(=)$	8.3	singlet
	$CH_3-C(CH_3)=CH-$	8.3	two singlets
Methylene	$-CH_2-CH_2-$	8.7	multiplet
	$-CH_2-CH=CH-$	7.9	multiplet
	$CH_3-CH_2-C(=)$	7.9	quartet
	$CH_2=CH-CH_2-C(=)$	7.3	doublet
Methine	$-CH-CH_2-$	8.5	multiplet
	$-CH-CH=$	7.8	multiplet
Olefin	$CH_2=CH-$	5.0	two doublets
	$CH_2=C(=)$	5.0	singlet
	$R-CH=C(R'')-R'$	3.0-5.0	---

*Values in ppm (tau) from tetramethylsilane

at about 5.0 ppm with a characteristic splitting pattern. The presence of cis- and trans-isomers of an alkadiene can be determined from the NMR spectra because each isomers has a slightly different spectra. The area of a NMR absorption is directly proportionate to the number of protons causing the absorption. A comparison of the area of the absorption due to each type of protons gives more confirming evidence for the structure of the dienes. Cywinski[34] used NMR data to determine the structures identical or similar to the alkadienes prepared in this research. The NMR of the alkadienes with identical structures as those analyzed by Cywinski had identical NMR data.

All the conjugated alkadienes have an absorption maxima in the U.V. above 210$m\mu$. In Table III are recorded λ_{max} and the ϵ_{max} recorded for each alkadiene, also the λ_{max} as calculated by Woodward's Rule[39] is included. Woodward's Rule predicting an absorption maximum at a longer wavelength for the more substituted diene does not hold for all the alkadienes studied. In two cases a more substituted conjugated alkadiene had an absorption at a shorter wavelength than a less substituted diene with the same carbon skeleton. 4-Ethyl-1,3-hexadiene (two alkyl substituents) had an absorption maxima at a higher wavelength than 3-ethyl-2,4-hexadiene (three alkyl substituents). Also 4-methyl-1,3-hexadiene had an absorption maxima at a higher wavelength than 3-methyl-2,4-hexadiene.

[39]H. Jaffe, and Milton Orchin, Theory and Applications of Ultraviolet Spectroscopy, John Wiley and Sons, New York, 1962, pp 196-204.

To calculate the wavelength of absorption maxima by Woodward's Rule, 5 $m\mu$ is added for each alkyl substitent on a diene to a basic unit of 217 $m\mu$. None of the unconjugated alkadienes had an absorption maxima above 210 $m\mu$.

TABLE III

Ultraviolet Absorption of Conjugated Alkadienes

Diene	λ_{max} Observed	ϵ_{max}	λ_{max} Calculated
1,3-octadiene	225.0	10,500	222
2,4-octadiene	228.5	11,200	227
4-ethyl-1,3-hexadiene	236.0	18,300	232
4-methyl-1,3-hexadiene	234.0	26,200	232
3-ethyl-2,4-hexadiene	232.0	22,400	237
3-methyl-2,4-hexadiene	231.0	23,100	237
2,5-dimethyl-2,4-hexadiene	242.0	25,200	242

Each alkadiene gave an IR spectrum with a unique absorption pattern which distinguished it from all the other alkadienes prepared. The infrared absorption frequencies in Table IV are those predicted for olefinic bonds[40]. Infrared absorption in the range 3095-3075 cm^{-1} can be used to identify terminal double bonds. If the above absorption is absent, an infrared absorption in the range 3040-3010 cm^{-1} indicates an internal double bond. The double bond (C=C vibration) at about 1640 cm^{-1} is absent if the double bond is at a center of symmetry, because this absorption requires a change in dipole moment. Trans-olefins which have an approximate center of symmetry such as trans-2-octene and trans-3-octene do not have an absorption at 1640 cm^{-1}, however, one would expect the corresponding cis-olefins to have an absorption. In conjugated dienes the C=C absorption becomes a doublet at about 1650 cm^{-1} and 1600 cm^{-1}, however, the peak heights are variable. In the case of a conjugated diene composed of isomers, more than one set of doublets can occur, e.g., the IR spectrum of 3-methyl-2,4-hexadiene (Spectrum #17, Appendix I). The trans-group (CH=CH) has a very characteristic absorption at about 965 cm^{-1}, however, the corresponding cis-group (CH=CH) occurs over a much larger wavelength region centered at about 670 cm^{-1}. The terminal olefinic group, $CR_1R_2=CH_2$, can be identified by an absorption at about 895-1750. The $CR_1R_2=CHR_3$ group has a characteristic

[40]L. J. Bellamy, The Infra-red Spectra of Complex Molecules, John Wiley and Sons, Inc., New York, 1954, pp 31-47.

TABLE IV

Infra-red Absorption Frequencies (cm^{-1})

Olefin carbon-carbon bonds		
Non-conjugated C=C		1680-1620 (v)
Conjugated C=C		1680-1620 (v)
		1630-1570 (v)
Olefinic carbon-hydrogen bonds		
trans	-CH=CH-	3040-3010 (m)
		970-960 (s)
cis	-CH=CH-	3040-3010 (m)
		690
Vinyl	$-CH=CH_2$	3095-3075 (m)
		3040-3010 (m)
		1856-1800 (m)
		1420-1410 (s)
		1300-1290
		995-985 (s)
		915-905 (s)
	$CR_1R_2=CH_2$	3095-3075 (m)
		1800-1750 (m)
		1420-1410 (s)
		895-885 (s)
	$CR_1R_2=CHR_3$	3040-3010 (m)
		840-790 (s)

absorption at 840-790 cm^{-1}. The IR spectra in Appendix I contain examples corresponding to the infrared absorption frequencies listed in Table IV. The IR spectra can be used to characterize and tentatively identify alkadienes. The IR coupled with the NMR data can adequately determine the structures of alkadienes prepared in this research.

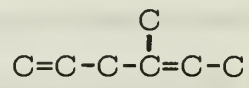
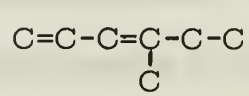
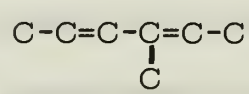
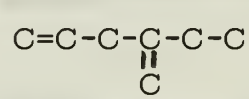
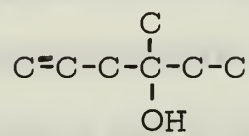
The preparation of unsaturated alcohols by the addition of an aldehyde to excess allyl magnesium chloride Grignard or by the addition of crotonaldehyde to excess n-butyl magnesium chloride Grignard gave good yields of the alcohols. The unsaturated alcohols contained small amounts of lower boiling contaminents which could be easily removed.

The dehydration of the unsaturated alcohols gave more unconjugated products than expected. Milas and McAlevy[28] reported an 88 per cent yield of dehydration products from 4-methyl-1-hexen-4-ol using sodium hydrogen sulfate. Their proof of the structure of the dehydration products to be 4-methyl-1,3-hexadiene was based upon the analysis of oxalic acid produced upon oxidation. The reduction products were oxidized for two days with alkaline potassium permanganate. They obtained 72 per cent of theoretical yield of oxalic acid from the oxidation. No other structure for the expected dehydration products except 4-methyl-1,3-hexadiene should be expected to yield oxalic acid upon oxidation.

When the dehydration of 4-methyl-1,hexene-4-ol with $NaHSO_4$ was carried out, four different dienes were found in the reduction

products. The composition of the reduction products is given below. In the dehydration of the unsaturated alcohol, 49 per cent of the product were 1,4-dienes, 26 per cent of the product was a 1,3-diene

Dehydration Products from 4-Methyl-1-hexene-4-ol

Compound		Per cent yield
4-methyl-1,4-hexadiene		39%
4-methyl-1,3-hexadiene		26%
3-methyl-2,4-hexadiene		12%
2-ethyl-1,4-pentadiene		10%
4-methyl-1-hexene-4-ol		12%

and 12 per cent of the product had a proton shift to give a 2,4-diene.

The 4-methyl-1,3-hexadiene and the 2-ethyl-1,4-pentadiene both partially rearranged to 4-methyl-1,4-hexadiene when sent for NMR analysis. This may have been caused by the acidic nature of the glass containers which had been cleaned with hot nitric acid. When ammonium hydroxide was used to rinse the glass containers before washing with distilled water and drying, 4-methyl-1,3-hexadiene did not rearrange in shipment for NMR analysis.

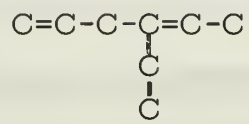
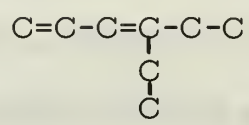
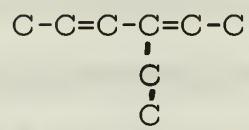
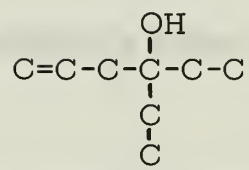
The 4-methyl-1,4-hexadiene appears to be the most favored diene under the conditions employed in the dehydration of 4-methyl-hexene-

4-ol. The most substituted olefinic bond is the one usually found to be most stable. Also a conjugated diene would be expected to be more stable than a non-conjugated diene. 4-Methyl-1,4-hexadiene may be favored over 4-methyl-1,3-hexadiene because of the "hyperconjugation" effect of the terminal methyl group in stabilizing the olefinic bond in the "4" position. The 3-methyl-2,4-octadiene would be expected to be the most thermodynamically stable diene formed in the reduction, since this diene is conjugated, the olefinic bonds are the most substituted and three methyl groups can help stabilize the double bond. However, 3-methyl-2,4-hexadiene had the undesirable property that it readily formed a colorless polymer even when stored in a refrigerator.

The dehydration of 4-ethyl-1-hexene-4-ol by sufuric acid was reported[30] in 1938 to give chiefly 4-ethyl-1,3-hexadiene with a small amount of 4-ethyl-1,4-hexadiene. The structure of the dienes was determined from an analysis of their oxidation products upon ozonolysis. Also the maleic anhydride addition product of the conjugated diene was also made. However, the same article cited an earlier experiment reported[41] in 1883 which determined the dehydration of 4-ethyl-1-hexen-4-ol with dilute sulfuric acid gave 4-ethyl-1,4-hexadiene. 4-Ethyl-1-hexen-4-ol was dehydrated in this research with $NaHSO_4$ in benzene to give the following distribution of products.

[41] S. Reformatski, Zh.R.H.O., 15, 518 (1883) cited by Ya. M. Slobodin, J. Gen. Chem. (U.S.S.R.), 8, 241-53 (1938).

Dehydration Products of 4-ethyl-1-hexene-4-ol

Compound		Per cent yield
4-ethyl-1,4-hexadiene		60%
4-ethyl-1,3-hexadiene		4.7%
3-ethyl-2,4-hexadiene		15.8%
starting material		19.5%

A much different distribution of dehydration products was found than the dehydrations of the same alcohols with sulfuric acid that were reported in the literature.[30,41] The early researchers did not report finding any of the 2,4-diene in their dehydration products.

The unconjugated 4-ethyl-1,4-hexadiene may be more thermodynamically stable than the conjugated 4-ethyl-1,3-hexadiene because of the stabilization from the "hyperconjugation" effect on the methyl group on the olefinic bond. The conjugated diene 3-ethyl-2,4-hexadiene should be the thermodynamically most stable diene produced in the reduction of 4-ethyl-1-hexene-4-ol since it has the most substituted double bond and two methyl groups adjacent to the double bond.

The dehydration of 2-octen-4-ol on aluminum oxide at 270°C was reported[31] to give 2,4-octadiene after distillation and purification of the reaction products, no other dienes were identified. When 2-octen-4-ol was dehydrated by passing over aluminum oxide at 270° in this research, both 1,3-octadiene and 2,4-octadiene were formed in almost equal amounts as given below.

Dehydration Products of 2-Octene-4-ol

Compound	Per cent yield
1,3-octadiene	49%
2,4-octadiene	50%
undetermined	~ 1%

The 2,4-octadiene should be thermodynamically more stable than 1,3-octadiene since in the first diene the olefinic bonds are more substituted and stabilized by a methyl group.

The alkyl substituted unsaturated alcohols 4-methyl-1-hexen-4-ol and 4-ethyl-1-hexen-4-ol were readily dehydrated using $NaHSO_4$, however, no dehydration with aluminum oxide at high temperatures were attempted. The unsaturated alcohols 2-octene-4-ol, 1-octene-3-ol and 1-decen-4-ol were not readily dehydrated by $NaHSO_4$ in boiling benzene. The dehydration of 1-octene-3-ol and 1-decen-4-ol by aluminum oxide at 270°C was not attempted, but these dienes will probably dehydrate under these conditions.

Good yields of conjugated dienes were not obtained on dehydration of the unsaturated alcohols 4-ethyl-1-hexen-4-ol and 4-methyl-1-

hexen-4-ol with $NaHSO_4$. Early researchers[28,30] determined good yields of conjugated dienes from these unsaturated alcohols were obtained using dehydrating agents such as sodium hydrogen sulfate, sulfuric acid and oxalic acid. However, these early investigators did not have the instrumental methods of analysis available today, i.e., infrared, ultraviolet, and nuclear magnetic resonance spectroscopy and gas chromatographic analysis. Their chemical methods of analysis were not suitable if complex mixtures of dienes resulted from the dehydration of unsaturated alcohols.

Many of the experiments of the dehydration of unsaturated alcohols reported in the literature seem to need reinvestigation. With the instrumental methods of analysis now available, the reduction products from the dehydration of unsaturated alcohols could be determined both more quickly and more accurately.

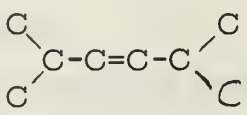
Dienes with different numbers of alkyl substituents were reduced with sodium-ammonia solutions. The reduction of 1,3-octadiene (mono-alkyl substituted), 2,4-octadiene (dialkyl substituted), 4-methyl-1-3-hexadiene (dialkyl substituted) and 2,5-dimethyl-2,4-hexadiene (tetraalkyl substituted) were investigated in this research.

2,5-Dimethyl-2,4-hexadiene was the alkadiene most extensively studied. In all but one of the reductions, methanol was used both as a protonating agent and to react with any sodium amide formed in the reaction. The reduction of 2,5-dimethyl-2,4-hexadiene by sodium-ammonia solutions was also investigated by Levina et al,[10] but under

much different reaction conditions. The reductions of 2,5-dimethyl-2,4-hexadiene including the two reported in the literature are summarized below.

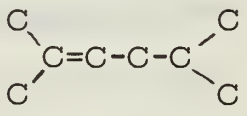
Reduction of 2,5-Dimethyl-2,4-hexadiene

Run 1 1.52g. diene
25 ml. ether
2.2 ml. MEOH
→ 2.0g. Na, 350 ml. NH_3, 15 min., -33° → NH_4Cl →



I
20%

+



II
80%

Run 2 7.62g. diene
50 ml. ether
11 ml. MEOH
→ 7.6g. Na, 500 ml. NH_3, 15 min., -33° → NH_4Cl → I 26% II 74%

Run 3 7.62g. diene
50 ml. ether
→ 7.6g. Na, 500 ml. NH_3, 11 ml. MEOH, 10 min., -33° → NH_4Cl → I 24% II 74%
Unreacted diene 2%

Run 4	7.6g. diene	7.6g. Na	NH_4Cl	I	II
	50 ml. ether	500 ml. NH_3		23%	77%
	11 ml. MEOH	5.2 hrs.			
		-33^{o}			
Run 5	15g. diene	24g. Na	NH_4Cl	I	II
	50 ml. ether	250 ml. NH_3		8% +	38%
		5 hrs.		unreacted diene	
		-33^{o}			
Lit.[10]	15g. diene	24 g. Na		II	
	ether	250 ml. NH_3			
		5-6 hrs.			
		-50^{o} to -60^{o}			
Lit.[10]	10g. diene	7g. Na		65% unreacted diene	
		250 ml. NH_3			
		5-6 hrs.			
		-50^{o} to -60^{o}			

In the sodium-ammonia reduction of 2,5-dimethyl-2,4-hexadiene, the addition of methanol greatly enhanced the rate of reaction. Methanol acted as a protonating agent more readily than the solvent ammonia. Methanol also reacts with any strong base formed in the reduction such as sodium amide. In the presence of methanol, a significant amount of the reduction product, 2,5-dimethyl-3-hexene, did not isomerize to 2,5-dimethyl-2-hexene when the reaction time was increased from 10 minutes to 5.2 hours.

The addition of ammonium chloride to the reaction mixture removed all the sodium dissolved in the ammonia, as indicated by the color change of the solution from dark blue to colorless. The ammonium chloride, a weak acid, also reacts with any strong base formed in the reduction, thus lessening the possibility of isomerization of reduction products.

The unsymmetrical olefin 2,5-dimethyl-2-hexene is probably more stable than the symmetrical olefin 2,5-dimethyl-3-hexene since the former olefin has more alkyl substituents on the double bond. The unsymmetrical olefin is probably additionly stabilized by the "hyper-conjugation" effects of the two methyl groups adjacent to the double bond.

When Levina et al reduced 2,5-dimethyl-2,4-hexadiene with a sodium-ammonia solution, they did not use any reagents such as methanol or ammonium chloride to remove strong bases formed in the reduction. They found only 2,5-dimethyl-2-hexene as a reduction product. If any 2,5-dimethyl-3-hexene was formed in their reaction, it may have isomerized to 2,5-dimethyl-2-hexene by strong bases present in the reaction mixture. It would be interesting to see if 2,5-dimethyl-3-hexene isomerized to 2,5-dimethyl-2-hexene under their reaction conditions. However, their analysis using Raman spectroscopy may not indicate 2,5-dimethyl-3-hexene if only a small amount is present.

In our work, we found 2,5-dimethyl-2-hexene, 2,5-dimethyl-3-hexene and 2,5-dimethyl-2,4-hexadiene could be very easily separated and collected with a 20 foot "SE-30" column on the Autoprep.

The impurity indicated by the NMR in 2,5-dimethyl-2-hexene could not be identified but may have been due to polymerization of the olefin. Unfortunately, immediate NMR analysis could not be performed as soon as the olefin was separated by the Autoprep.

1,3-Octadiene was reduced with a sodium-ammonia solution. The two reductions of the diene are summarized below.

Reduction of 1,3-Octadiene

Run 1	0.75g. diene	1g. Na	5g. NH_4Cl	
	25 ml. ether	1.1 ml. MEOH		$\sim$ 25% 2-octene
		300 ml. NH_3		$\sim$ 75% polymer
		10 min.		
Run 2	2.0g. diene	2g. Na	10g. NH_4Cl	
	25 ml. ether	300 ml. NH_3		$\sim$ 25% monomer
	3 ml. MEOH	10 min.		$\sim$ 75% polymer

In Run 1, the monomeric reduction products of 1,3-octadiene were identified as 2-octene by both IR and NMR spectra. However, in Run 2, the mixture of monomeric reaction products could not be completely identified. The monomeric product contained 2-octene and some unidentified product which may be 3-octene. 1-Octene was not found as a reduction product of 1,3-octadiene.

In the sodium-ammonia reduction of 2,4-octadiene, the monomeric products could not be positively identified. The monomeric products were not 2-octene but may have been 3-octene and 4-octene. IR and NMR analysis by themselves cannot adequately distinguish between 3-octene and 4-octene, especially when both olefins are present together.

In the sodium-methanol-ammonia reductions of 1,3-octadiene and 2,4-octadiene, poor yields of monomers were obtained because much of the reaction products were polymeric. Levina et al.[9] reported a 75 per cent yield of monomeric reduction products of 2,4-hexadiene when the reduction was carried out at lower temperatures in the absence of methanol. It is possible that the sodium-ammonia reduction of 1,3-octadiene or 2,4-octadiene may give much better yields of monomers if different reaction conditions are used.

Some of the monomeric reduction products may have been carried out of the system by the ammonia when it distilled from the system. Most of the 50 ml. of ether used as solvent was lost from the system when 500 ml. of ammonia was evaporated overnight through a mercury trap. A significant amount of reduction products probably could be recovered from the gaseous ammonia as it leaves the system. In the reduction of the seven-carbon diene 4-methyl-1,3-hexadiene, the monomeric reduction products may have been lost when the ammonia distilled from the system. Monomeric reduction products of eight-carbon dienes have higher boiling than corresponding seven-carbon dienes which was advantageous in the experimental workup.

The method of running the Birch Reduction of alkadienes can greatly influence the distribution of reduction products as evidenced in the reduction of 2,5-dimethyl-2,4-hexadiene. No new mechanistic conclusions are evident from the results on the reduction of alkadienes obtained in this research. One surprising result was the indication by NMR spectra of the formation of about equal amounts of cis- and trans-2,5-dimethyl-3-hexene from the reduction of 2,5-dimethyl-2,4-hexadiene.

ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to his research advisor, Dr. Carlos G. Cardenas, whose support and encouragement were most helpful.

The author also wishes to express his gratitude to Dr. Charles P. Rowell and Dr. Glem Spencer--their aid was most helpful.

Gratitude to the United States Navy for the opportunity to attend this institution and complete the research is gratefully expressed.

Thanks is also due Mr. Donald W. Moore in producing the NMR spectra which were so necessary in this research.

The author would also like to express his thanks to Dr. John M. Hoffmann, Lieutenant Donald Kimble, Miss Carita M. Brane and Chief Yeoman F. Sanchez for their help in this work.

To his wife, Carol, and their children, this thesis is dedicated.

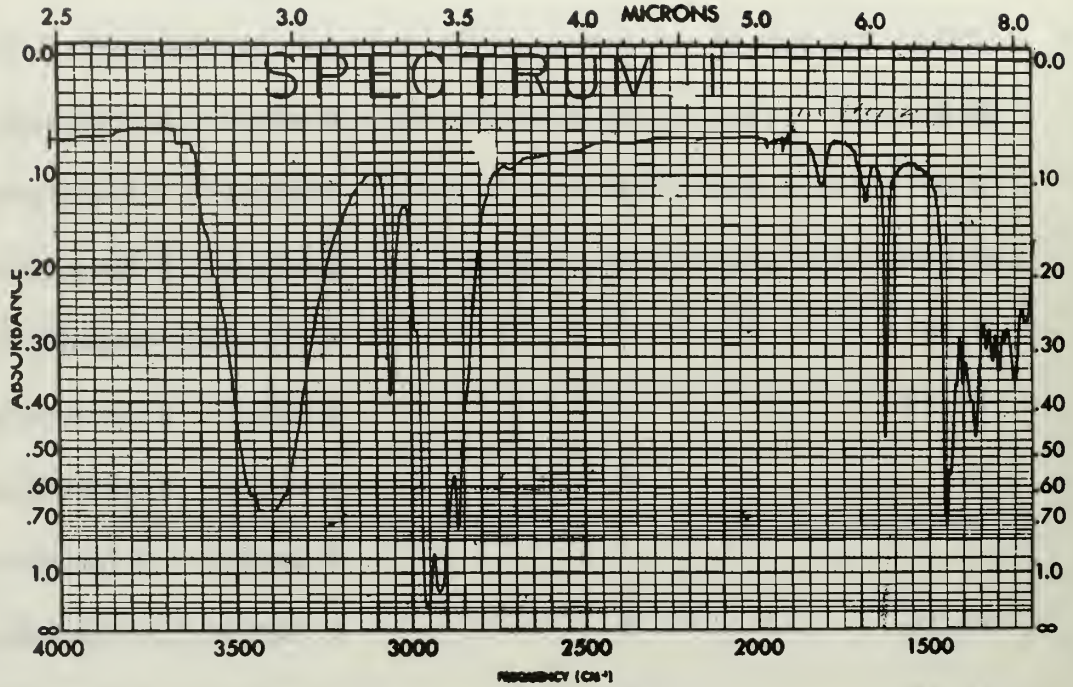
APPENDIX I

The infrared spectra found in this Appendix were recorded on a Perkin-Elmer Grating Infrared Spectrophotometer, Model 337. All liquids were done neat between sodium chloride disks. Calibration marks on some spectra are absorptions of a polystyrene film.

The table of contents for Appendix I and Appendix II is given on the following page.

Table of Contents for Appendices I and II

IR Spectrum # Appendix I	NMR Spectrum # Appendix II	Compound
1,2	-	4-ethyl-1-hexen-4-ol
3,4	1	4-ethyl-1,4-hexadiene
5,6	2	4-ethyl-1,3-hexadiene
7,8	3	3-ethyl-2,4-hexadiene
9,10	-	4-methyl-1-hexene-3-ol
11,12		2-ethyl-1,4-pentadiene
--	4	2-ethyl-1,4-pentadiene and 4-methyl-1,4-hexadiene
13,14	5	4-methyl-1,4-hexadiene
15,16	6	4-methyl-1,3-hexadiene
17,18	7	3-methyl-2,4-hexadiene
19,20	-	2-octene-4-ol
21,22	8	1,3-octadiene
23,24	9	2,4-octadiene
25,26	10	2,5-dimethyl-3-hexene
27,28	11	2,5-dimethyl-2-hexene
29,30	12	reduction product of 1,3-octadiene identified as 2-octene
31,32	-	reduction product of 1,3-octadiene
33,34	13	reduction product of 2,4-octadiene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.50
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.70
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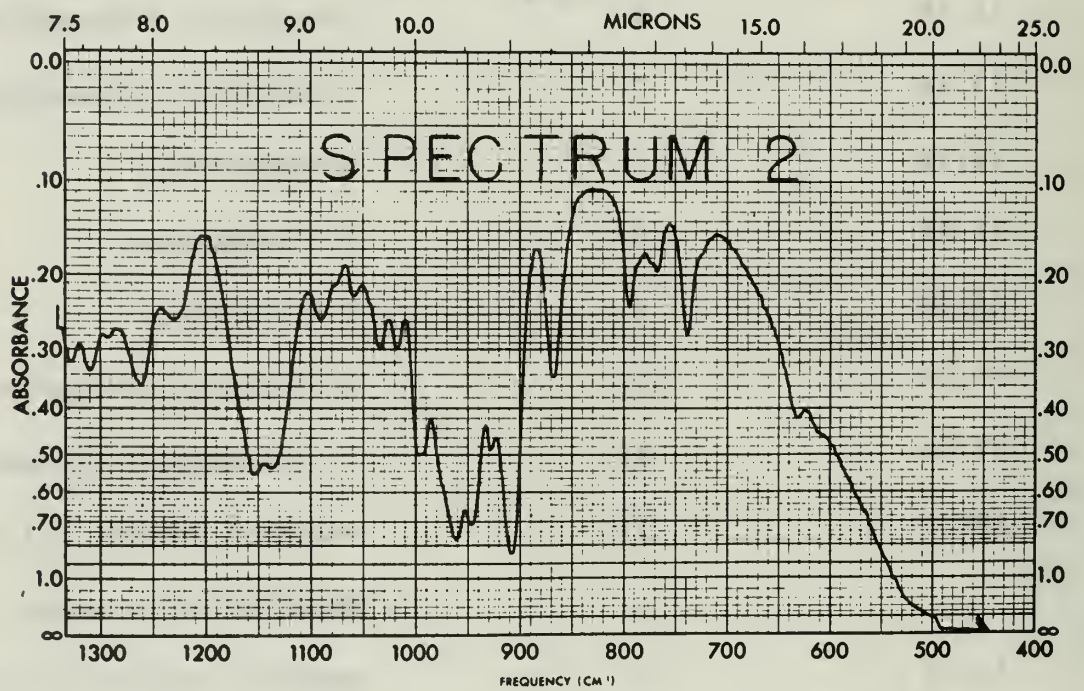
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.40
.50
.60
.70
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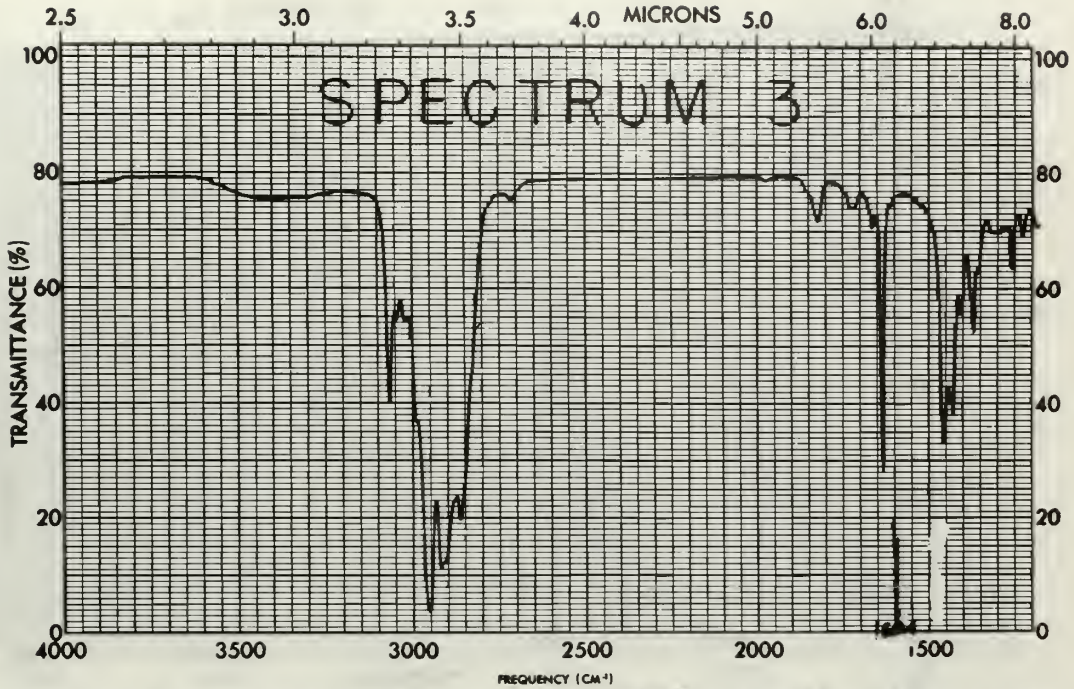
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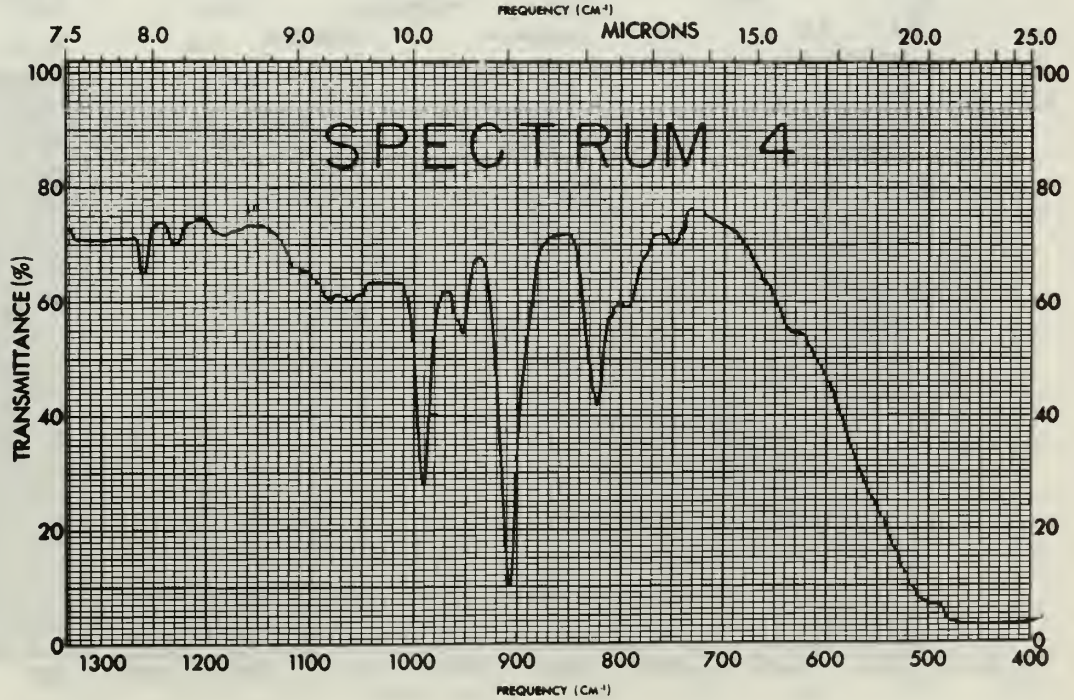
FREQUENCY (CM⁻¹)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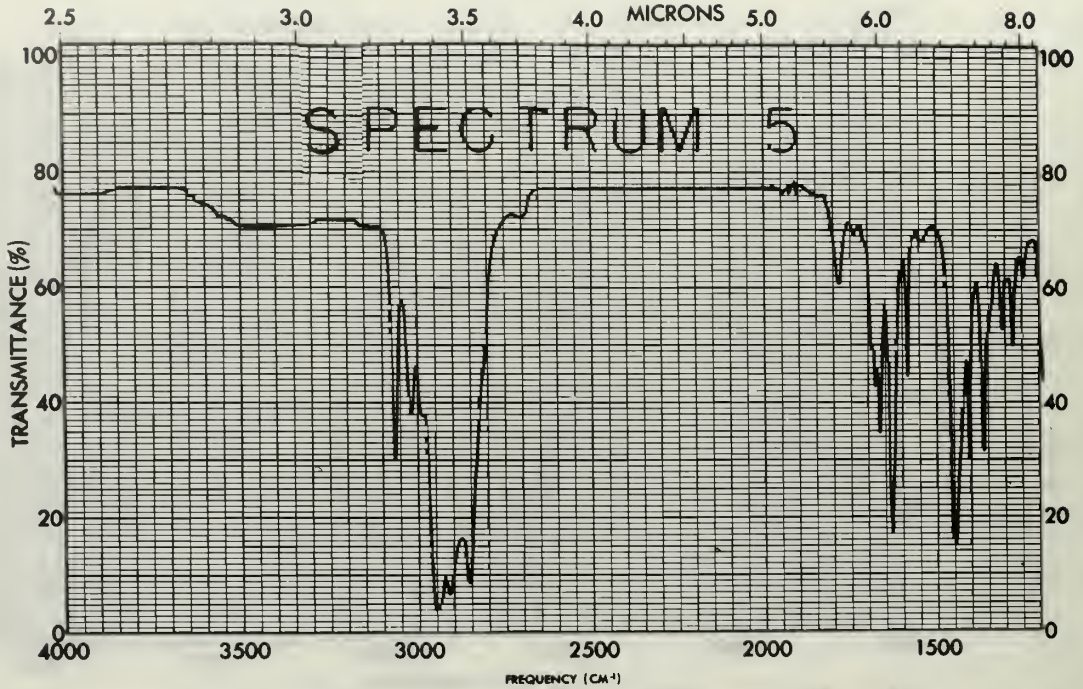
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1500
FREQUENCY (CM⁻¹)

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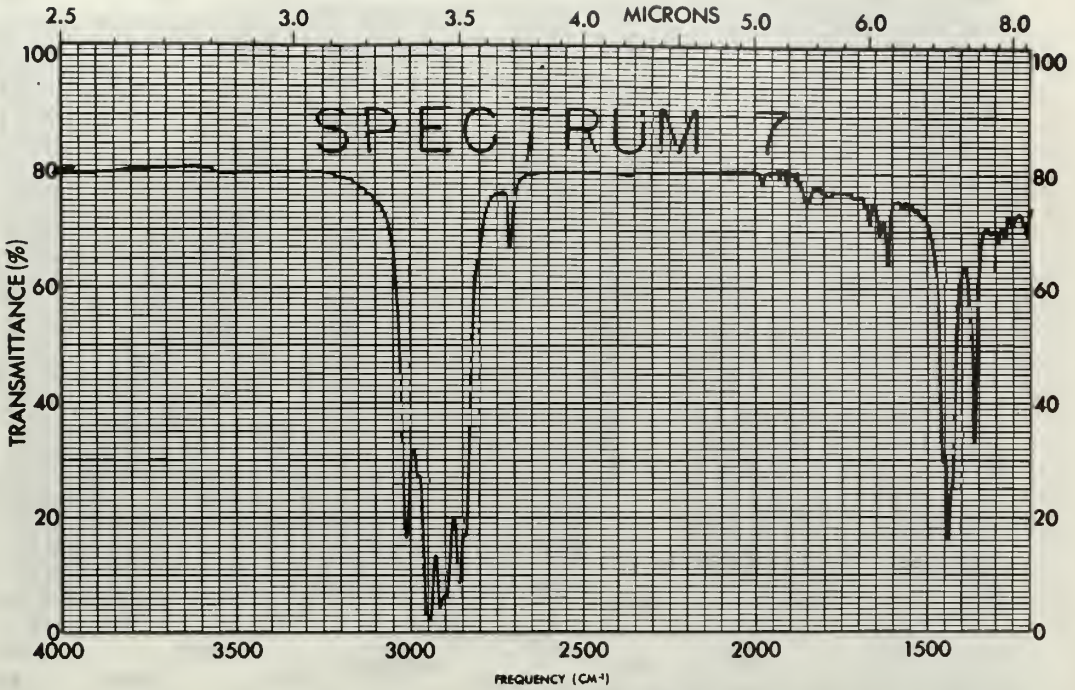
FREQUENCY (CM⁻¹)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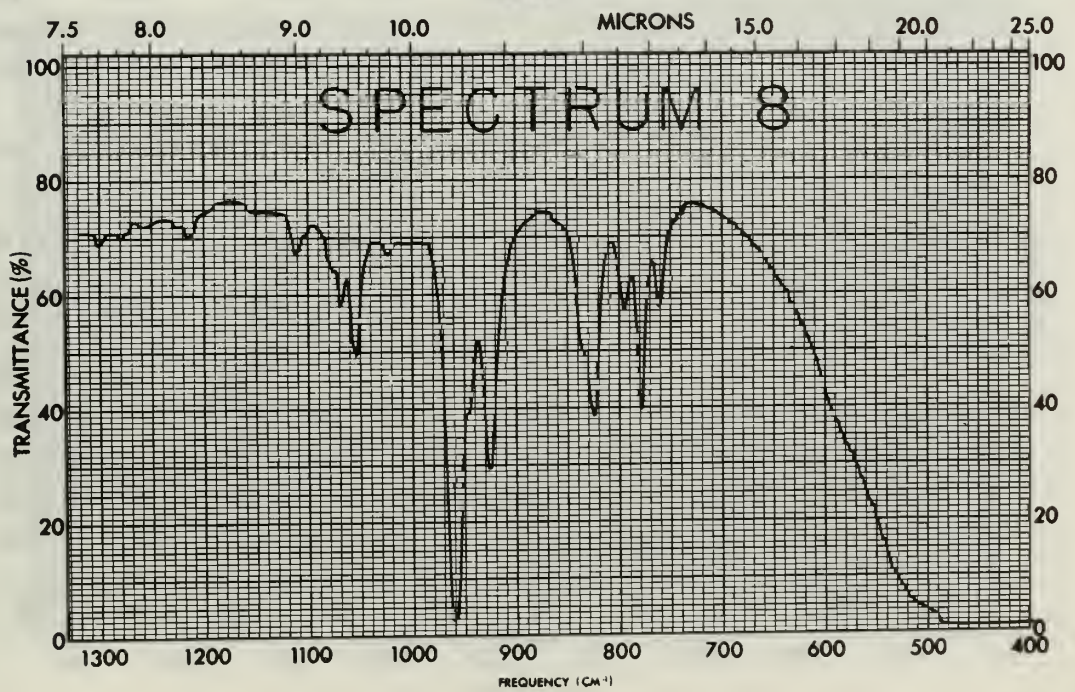
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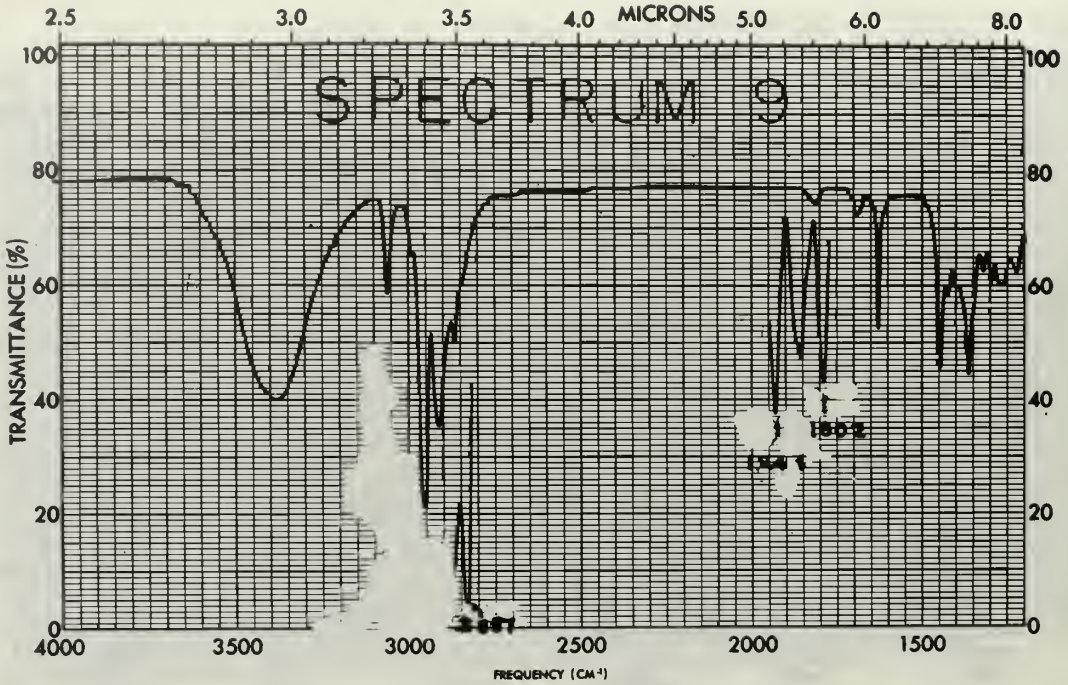
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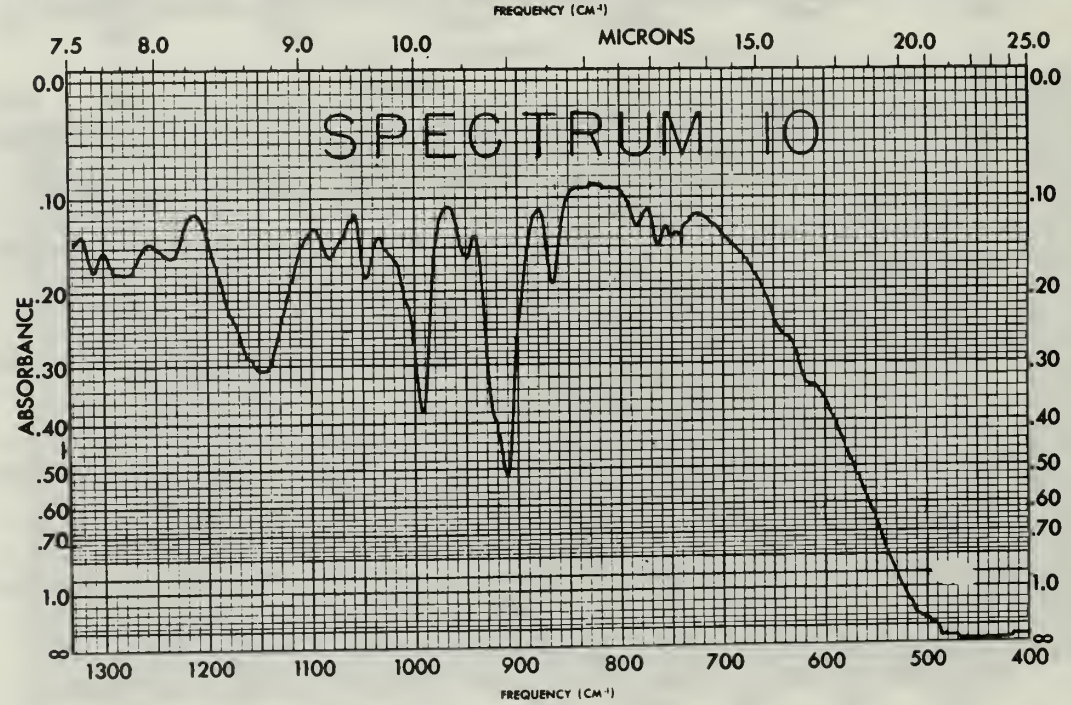
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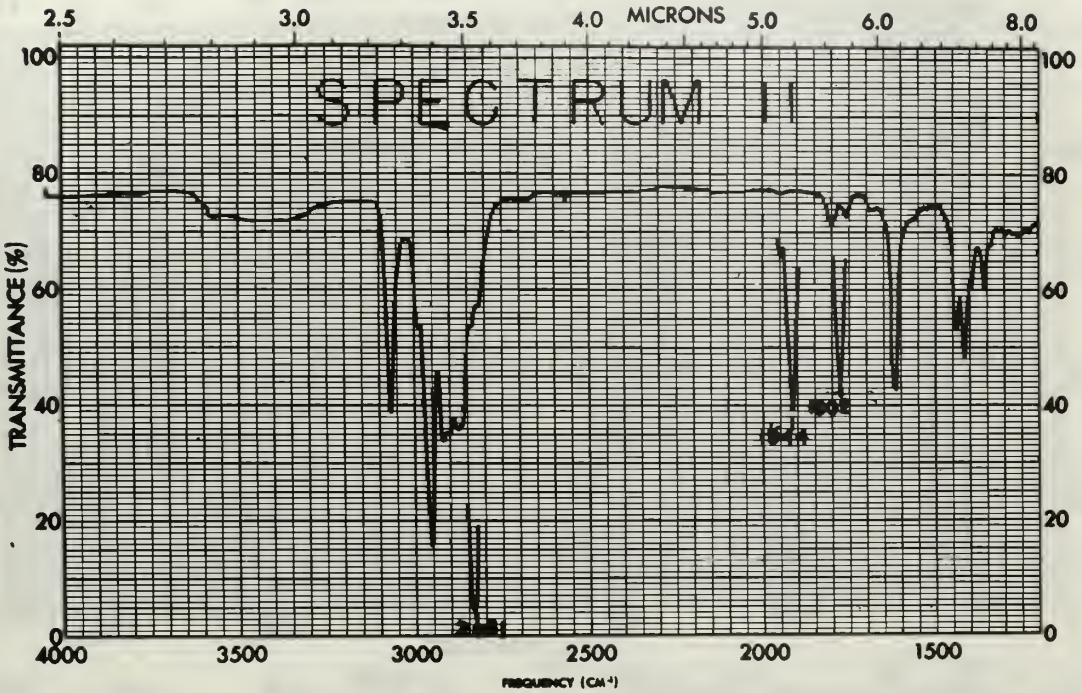
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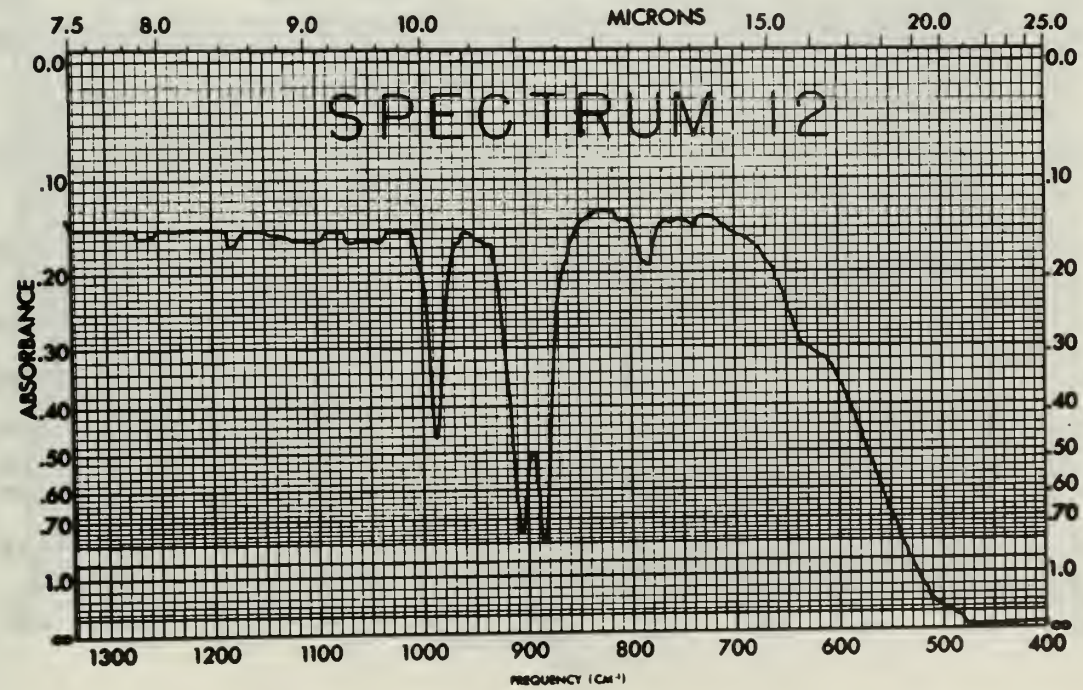
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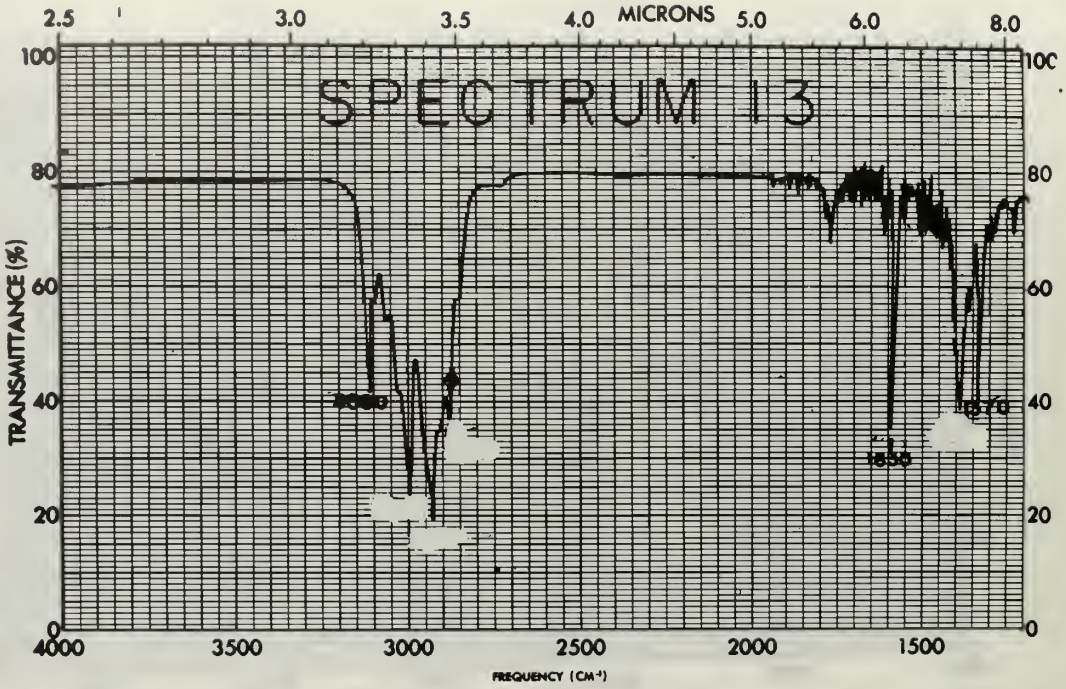
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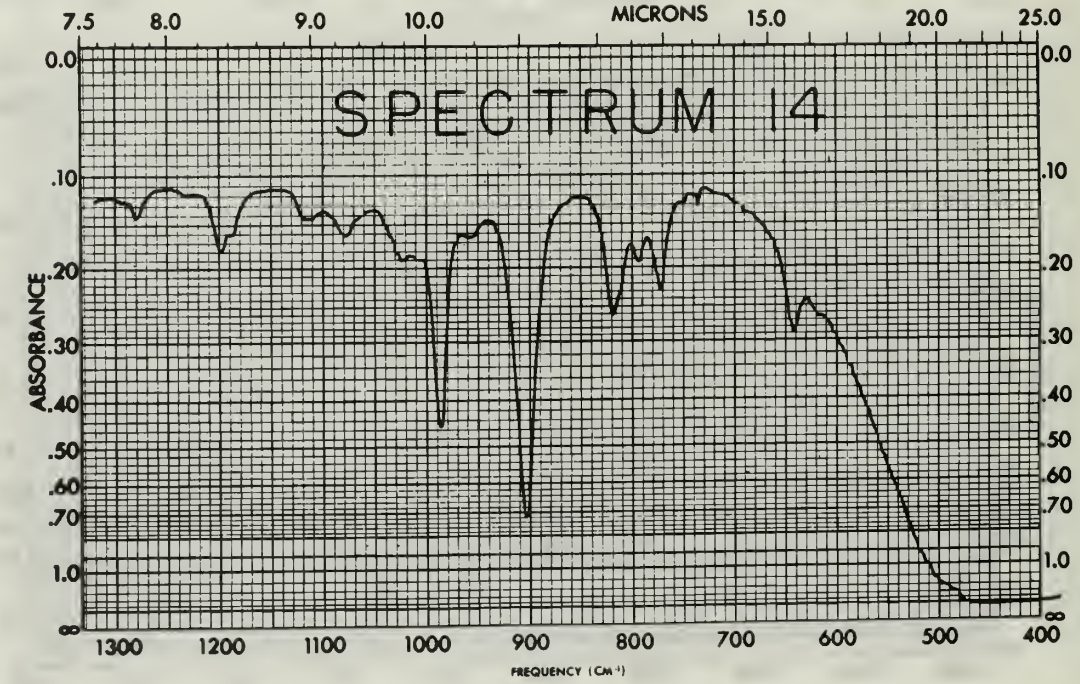
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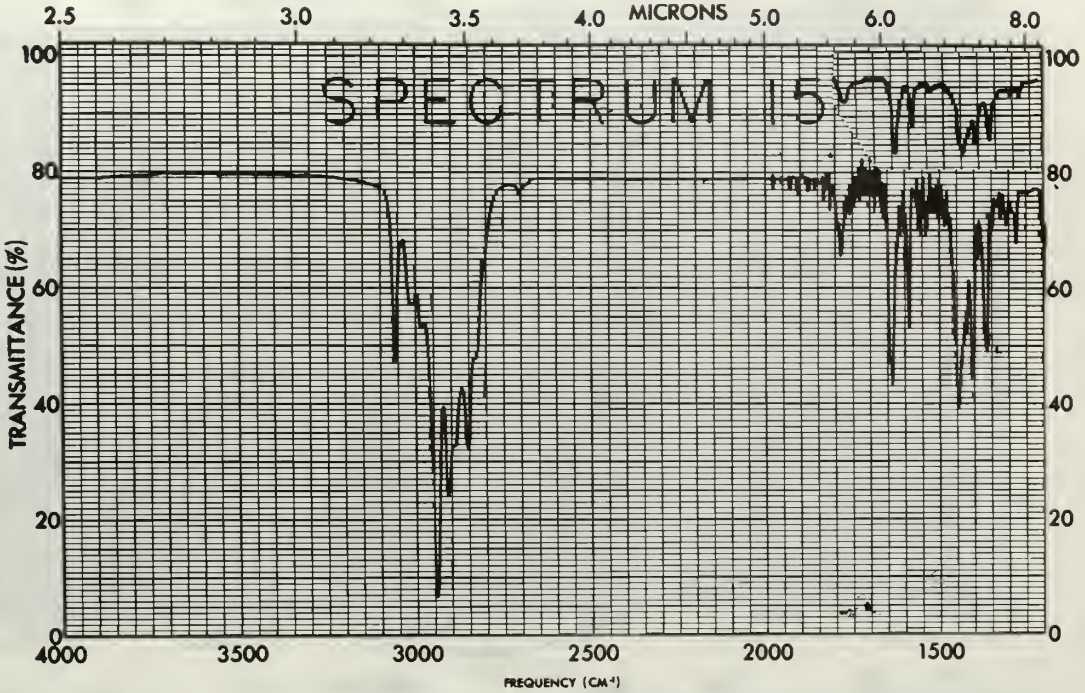
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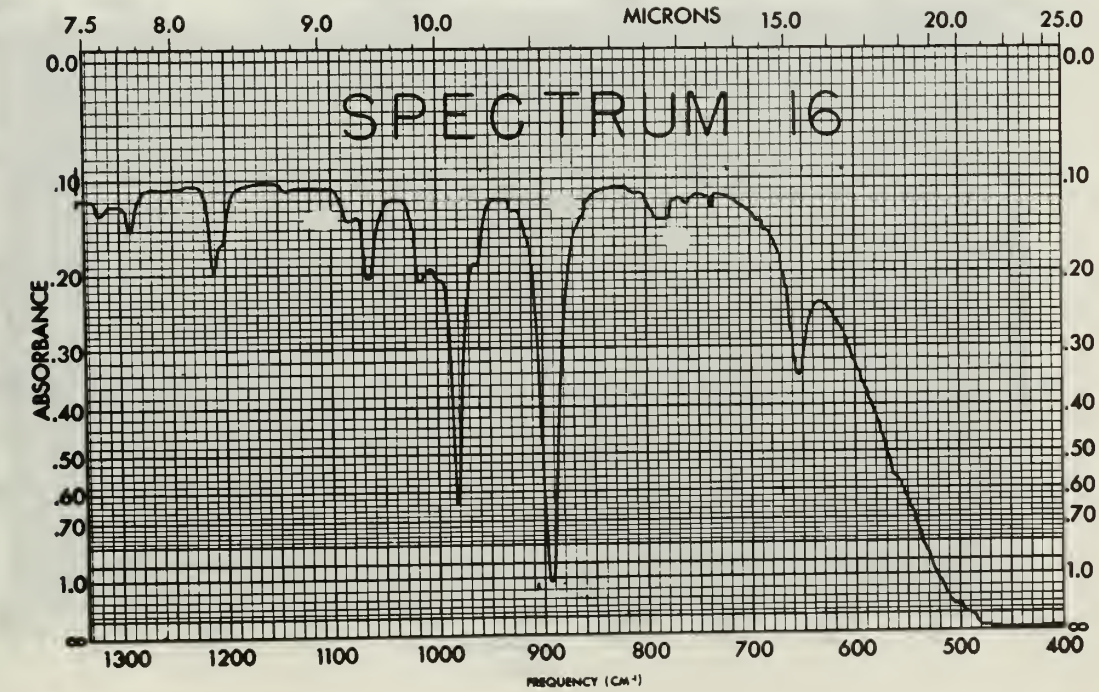
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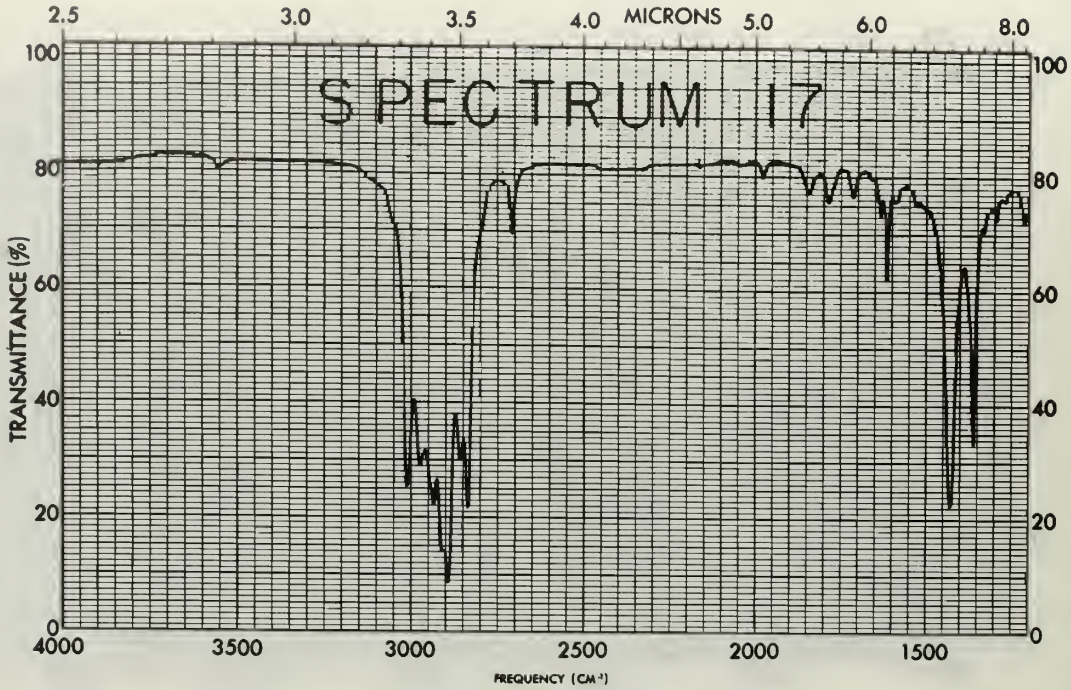
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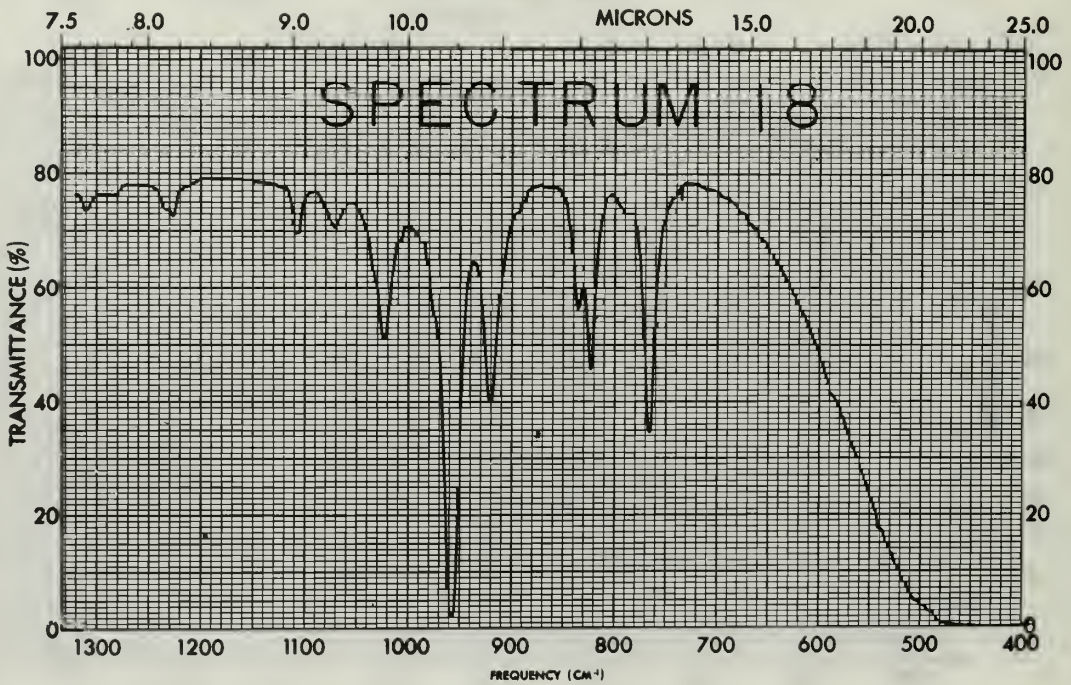
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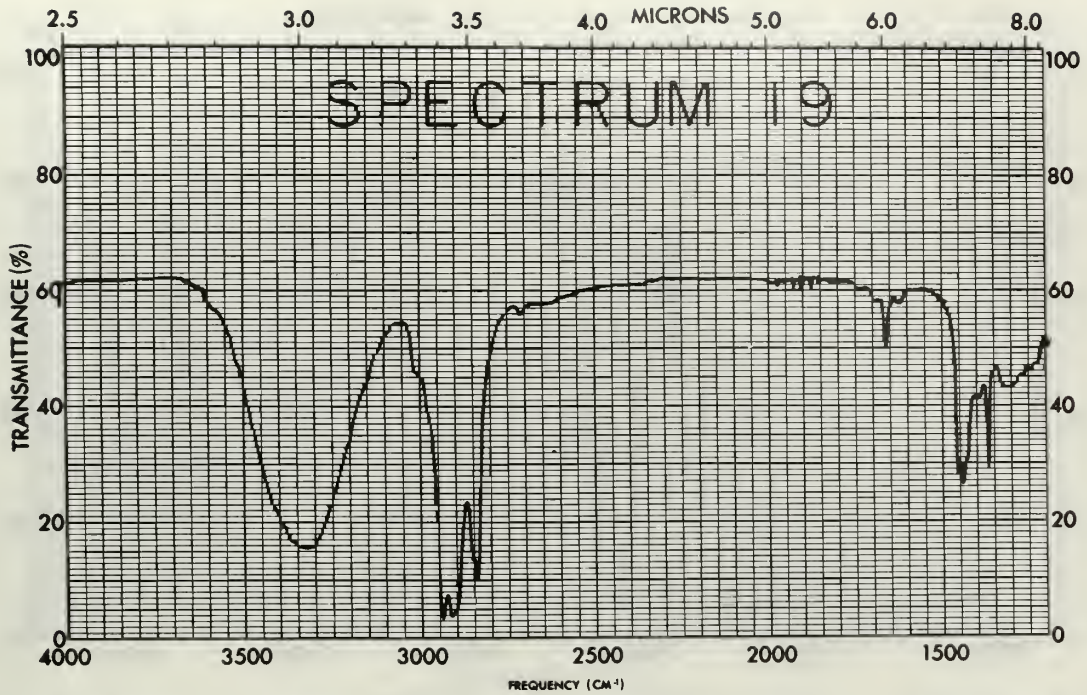
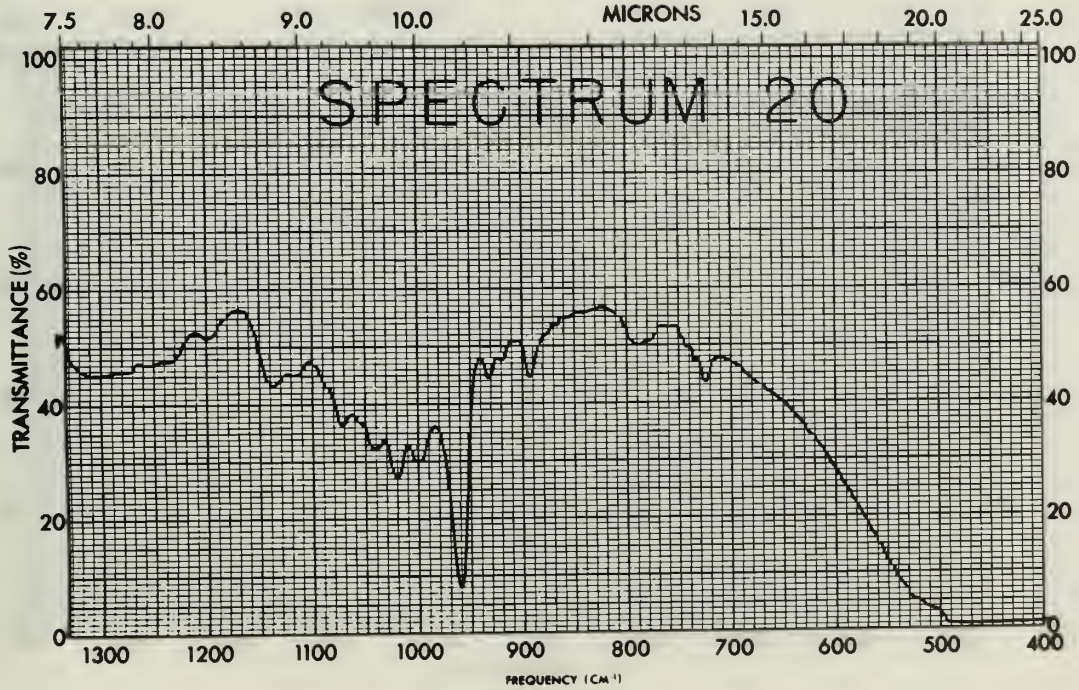
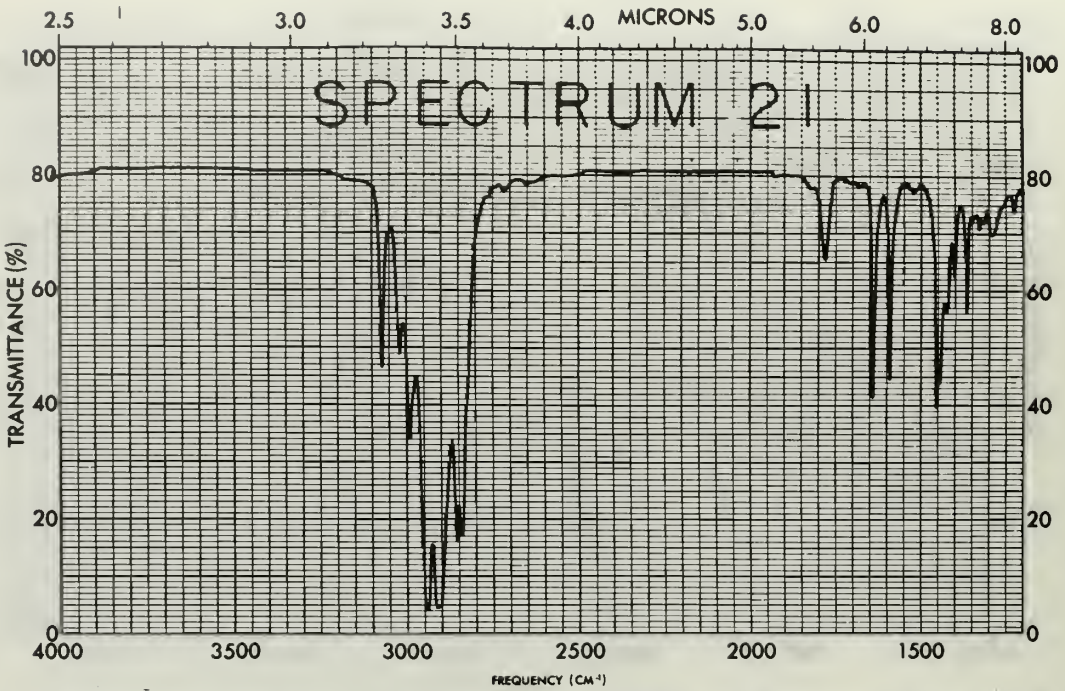
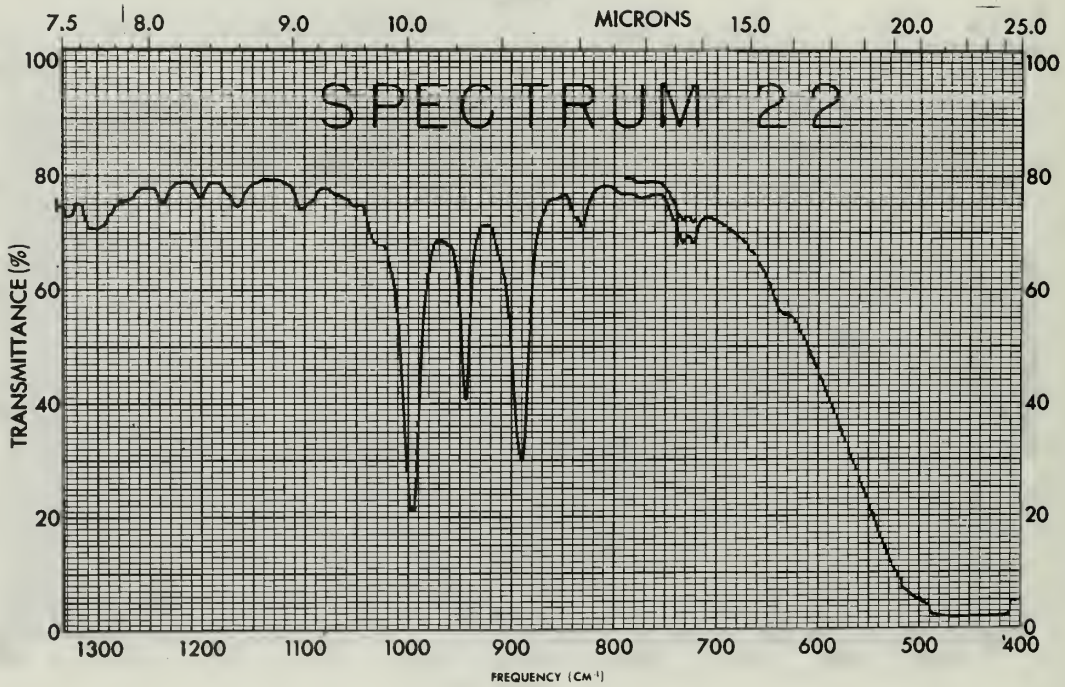
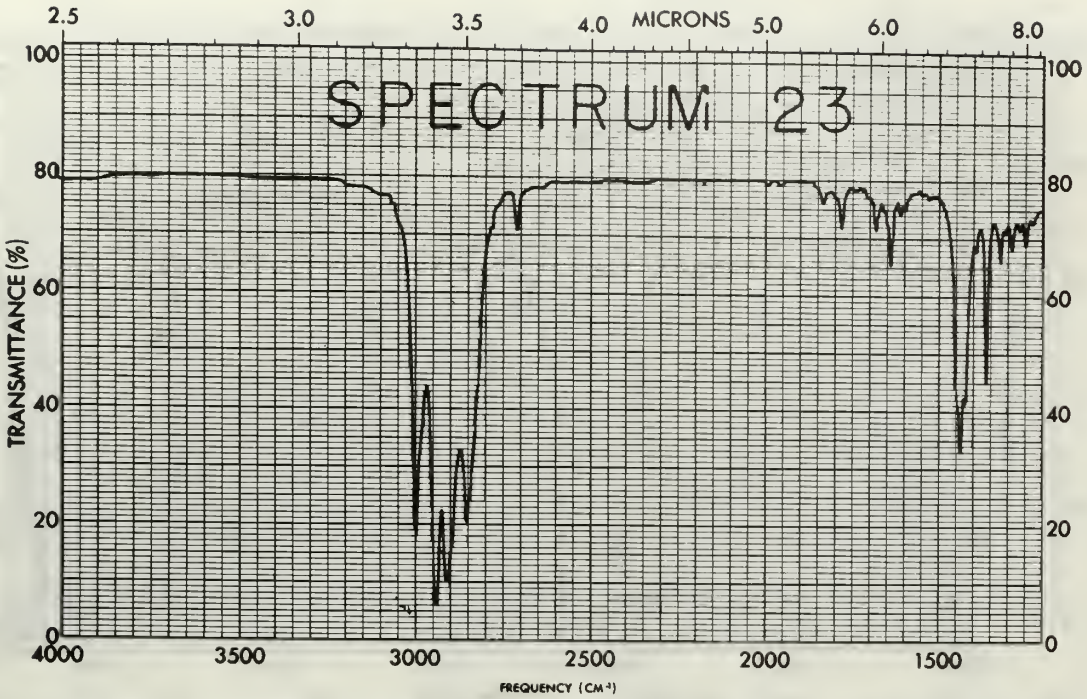
1000
900
800
700
600
500
400
FREQUENCY (CM⁻¹)

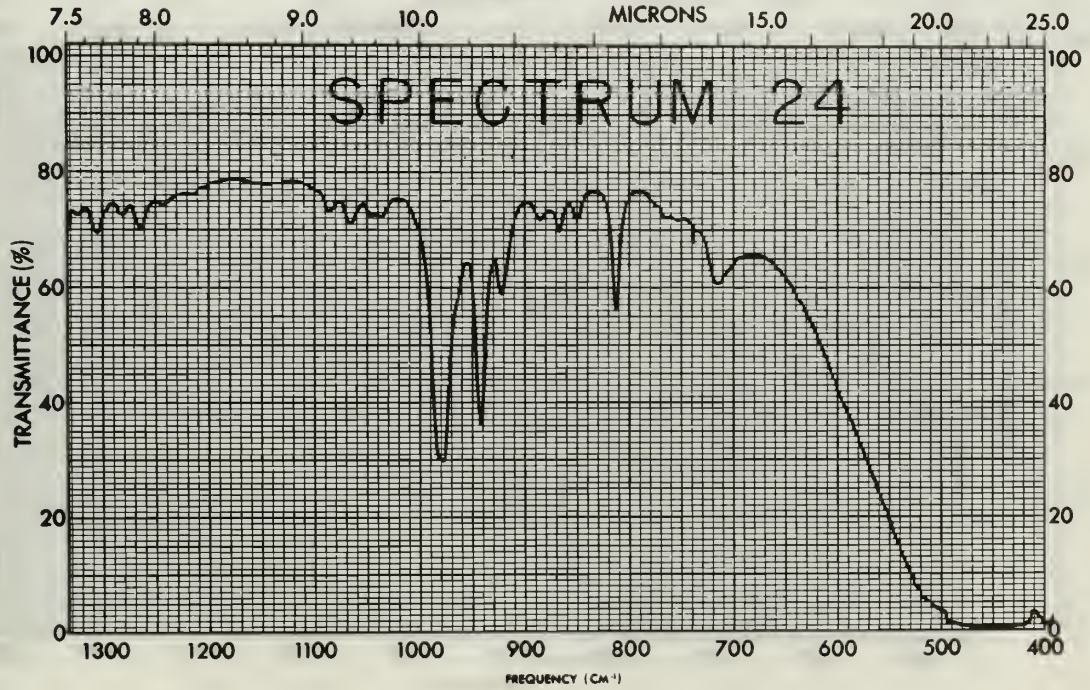

SPECTRUM 19
MICRONS
2.5
3.0
3.5
4.0
5.0
6.0
8.0
TRANSMITTANCE (%)
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
FREQUENCY (CM⁻¹)

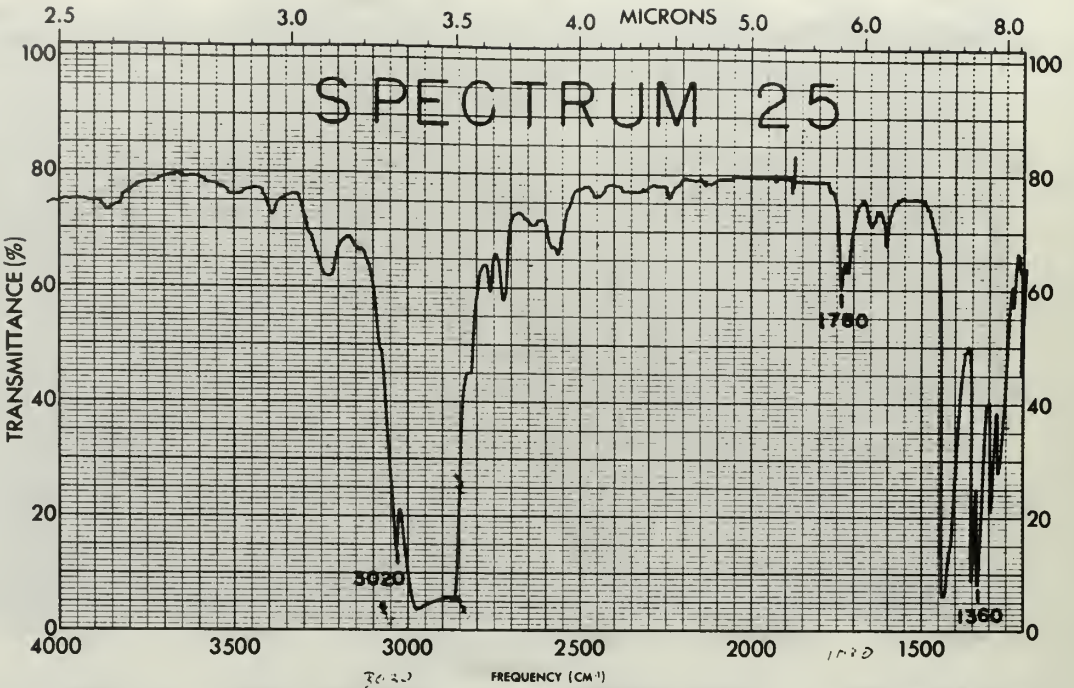

SPECTRUM 20
MICRONS
7.5
8.0
9.0
10.0
15.0
20.0
25.0
TRANSMITTANCE (%)
100
80
60
40
20
0
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (CM⁻¹)


SPECTRUM 21
MICRONS
2.5
3.0
3.5
4.0
5.0
6.0
8.0
TRANSMITTANCE (%)
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
FREQUENCY (CM⁻¹)


SPECTRUM 22
MICRONS
7.5
8.0
9.0
10.0
15.0
20.0
25.0
TRANSMITTANCE (%)
100
80
60
40
20
0
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (CM⁻¹)


SPECTRUM 23
MICRONS
2.5
3.0
3.5
4.0
5.0
6.0
8.0
TRANSMITTANCE (%)
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
FREQUENCY (CM⁻¹)


SPECTRUM 24
MICRONS
7.5
8.0
9.0
10.0
15.0
20.0
25.0
TRANSMITTANCE (%)
100
80
60
40
20
0
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (CM⁻¹)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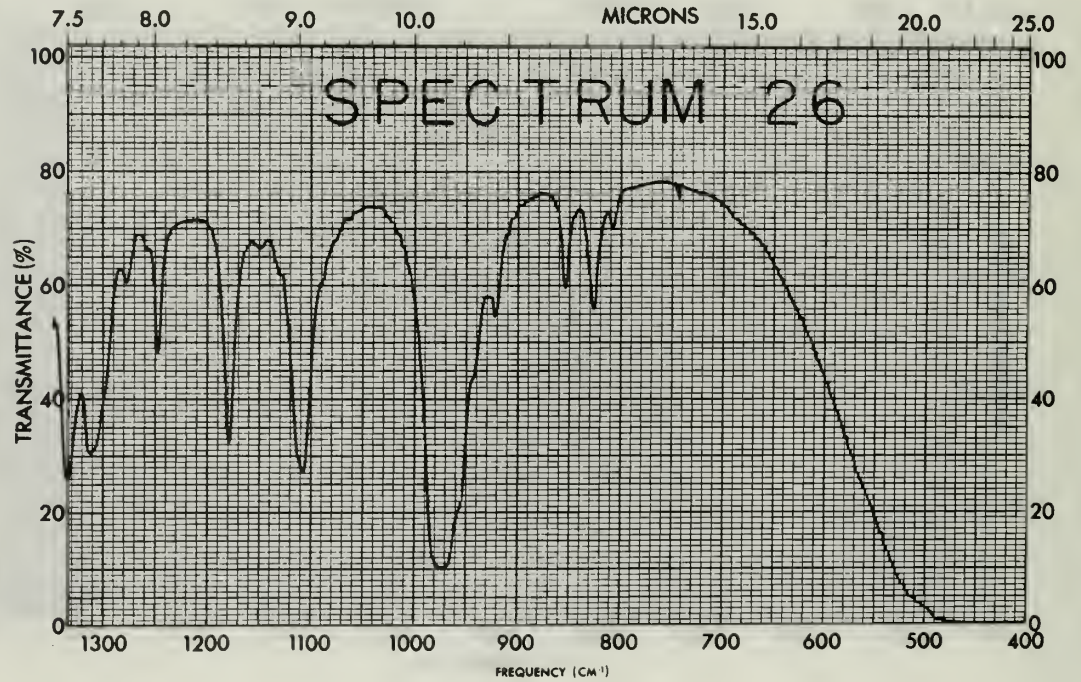
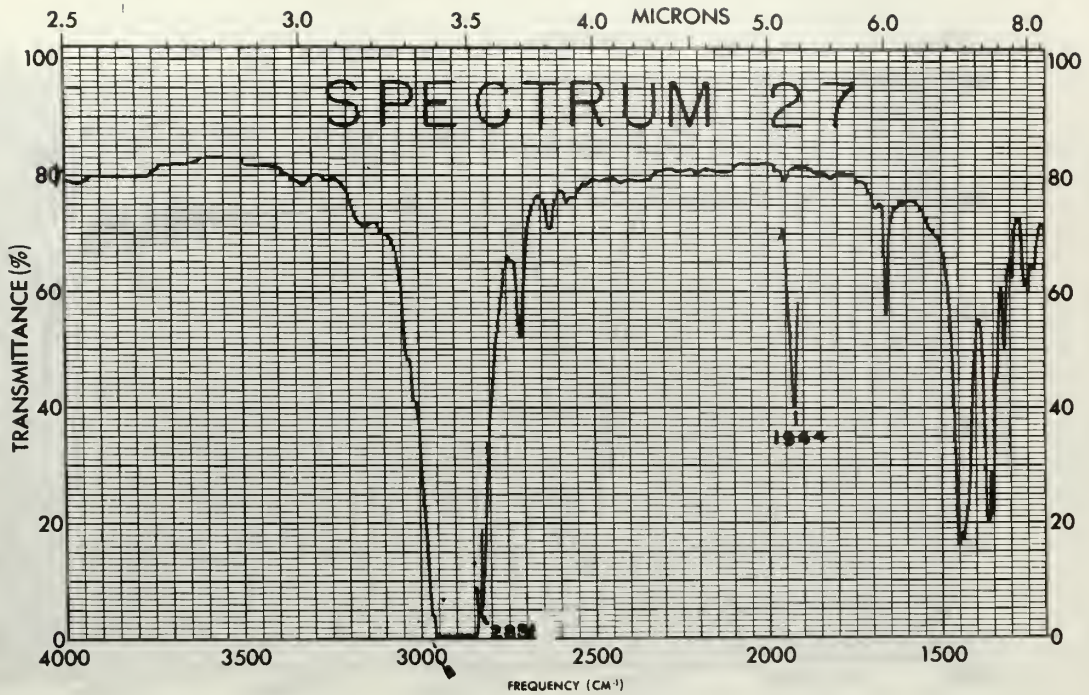
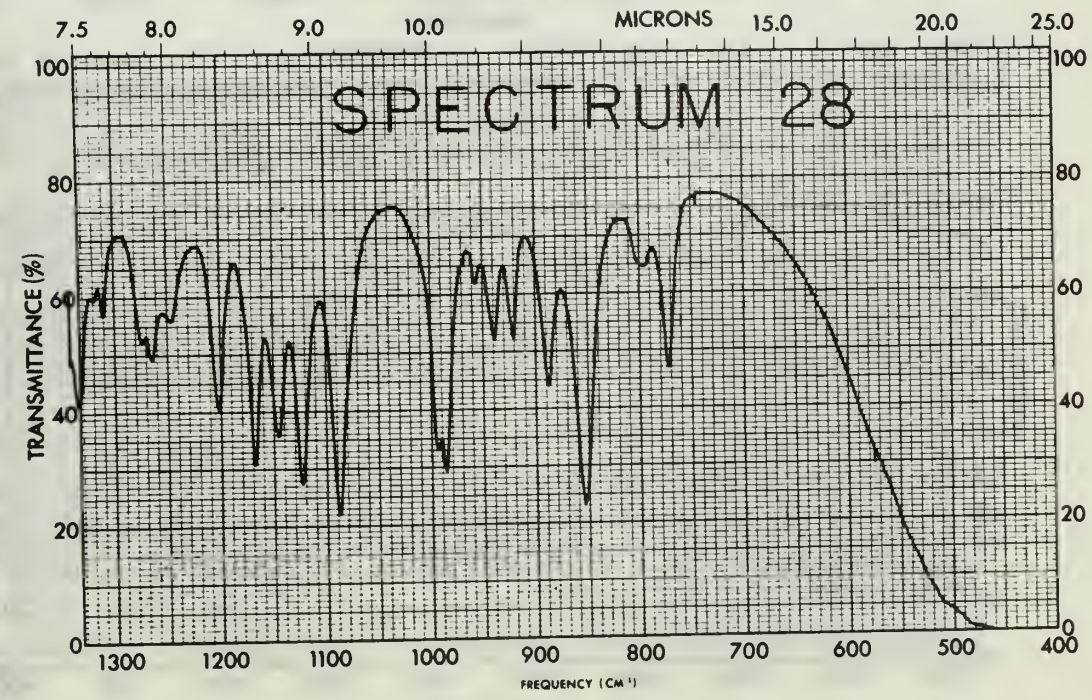
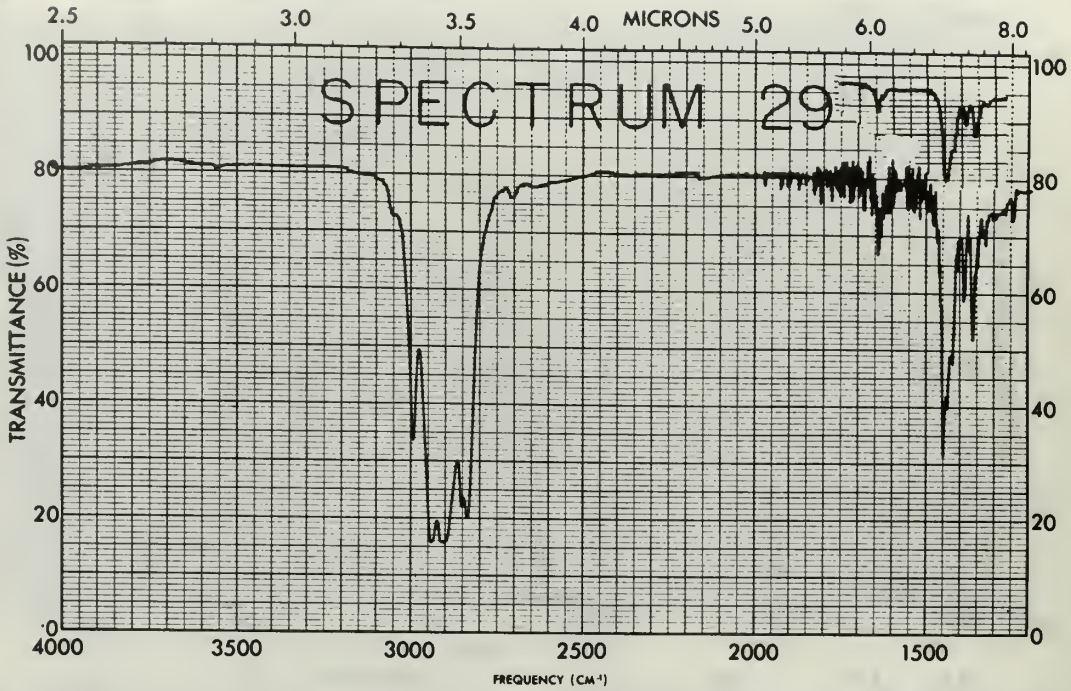
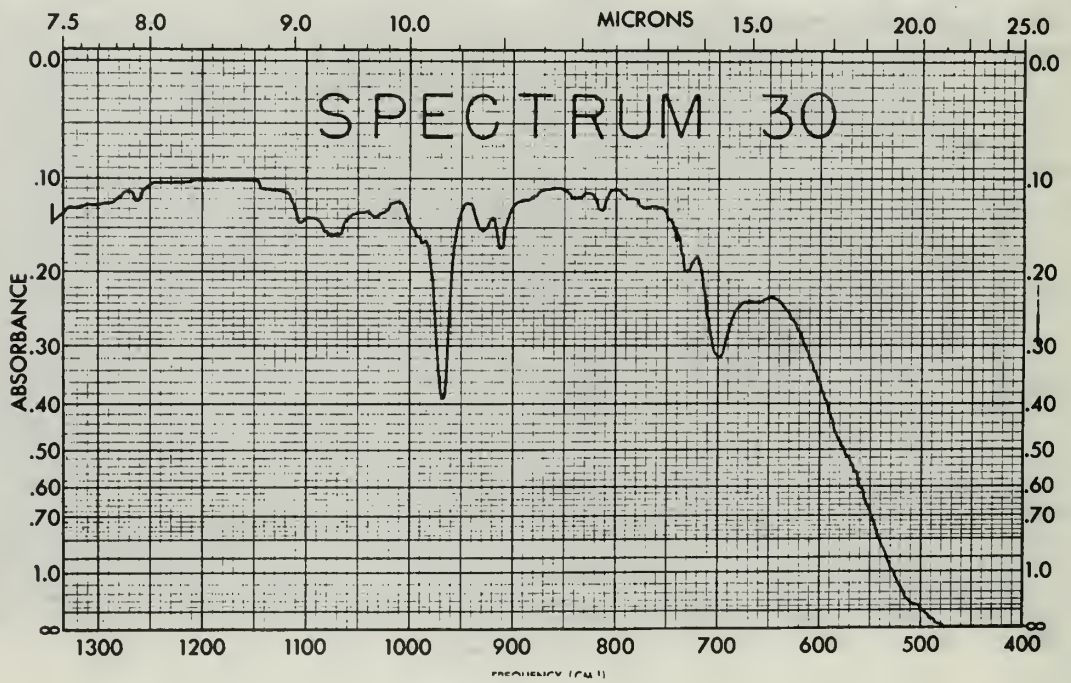
MICRONS
2.5
3.0
3.5
4.0
5.0
6.0
8.0
TRANSMITTANCE (%)
100
80
60
40
20
0
3020
1780
1360
4000
3500
3000
2500
2000
1500
FREQUENCY (CM⁻¹)

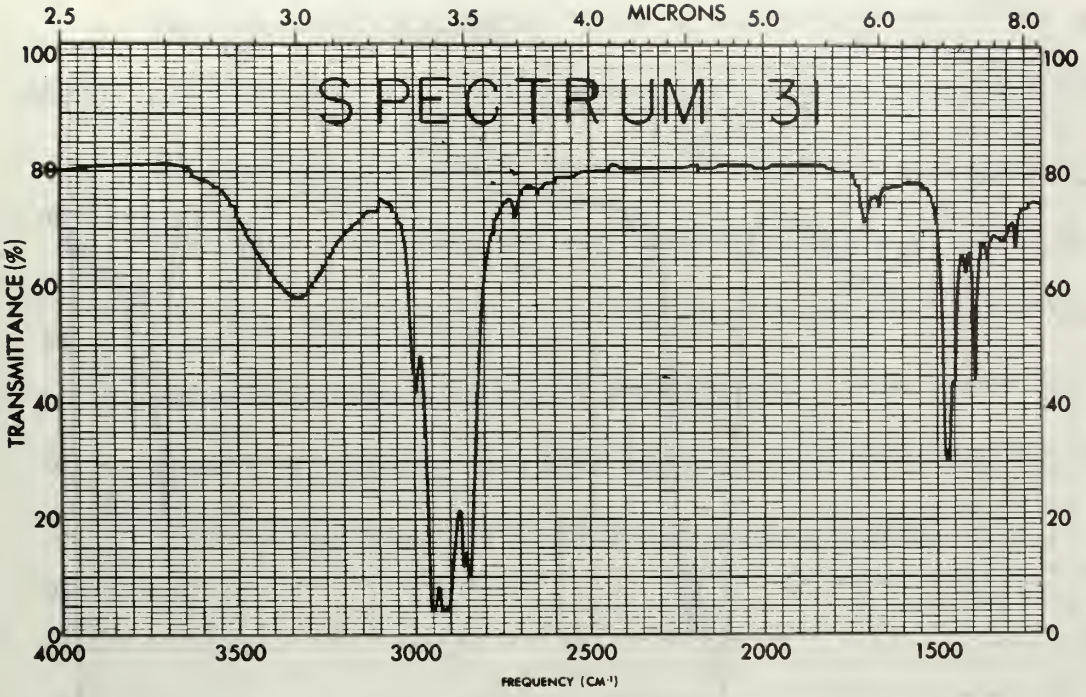

SPECTRUM 26
MICRONS
7.5
8.0
9.0
10.0
15.0
20.0
25.0
TRANSMITTANCE (%)
100
80
60
40
20
0
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (CM⁻¹)

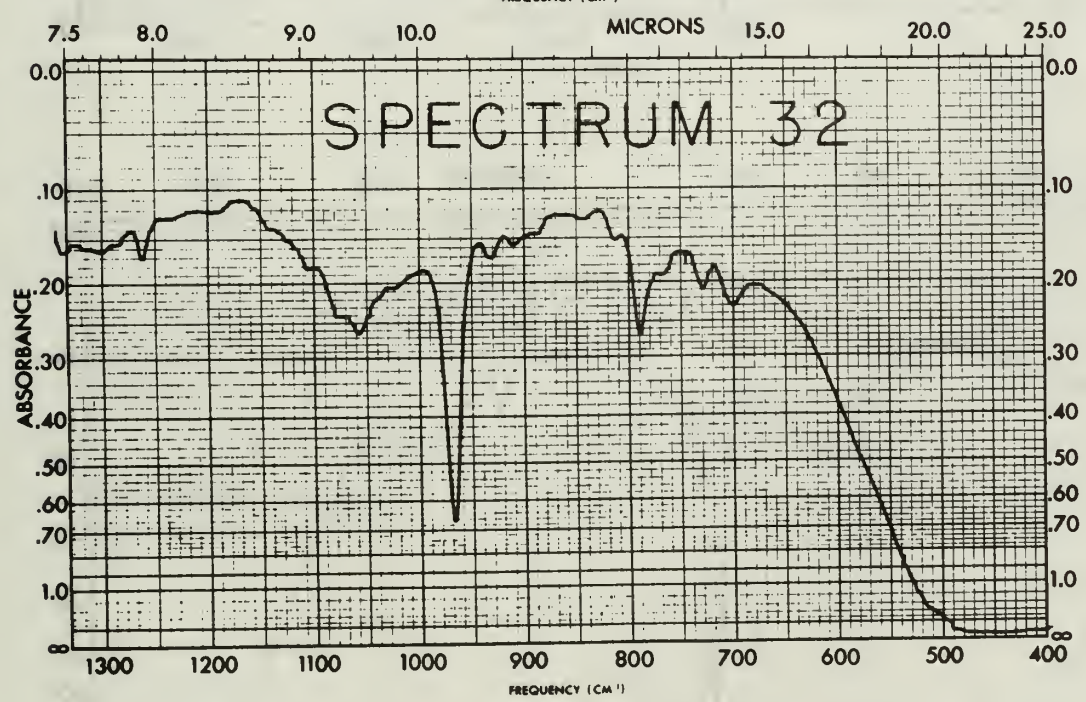

SPECTRUM 27
2.5
3.0
3.5
4.0
MICRONS
5.0
6.0
8.0
100
80
60
40
20
0
TRANSMITTANCE (%)
4000
3500
3000
2500
2000
1500
FREQUENCY (CM⁻¹)

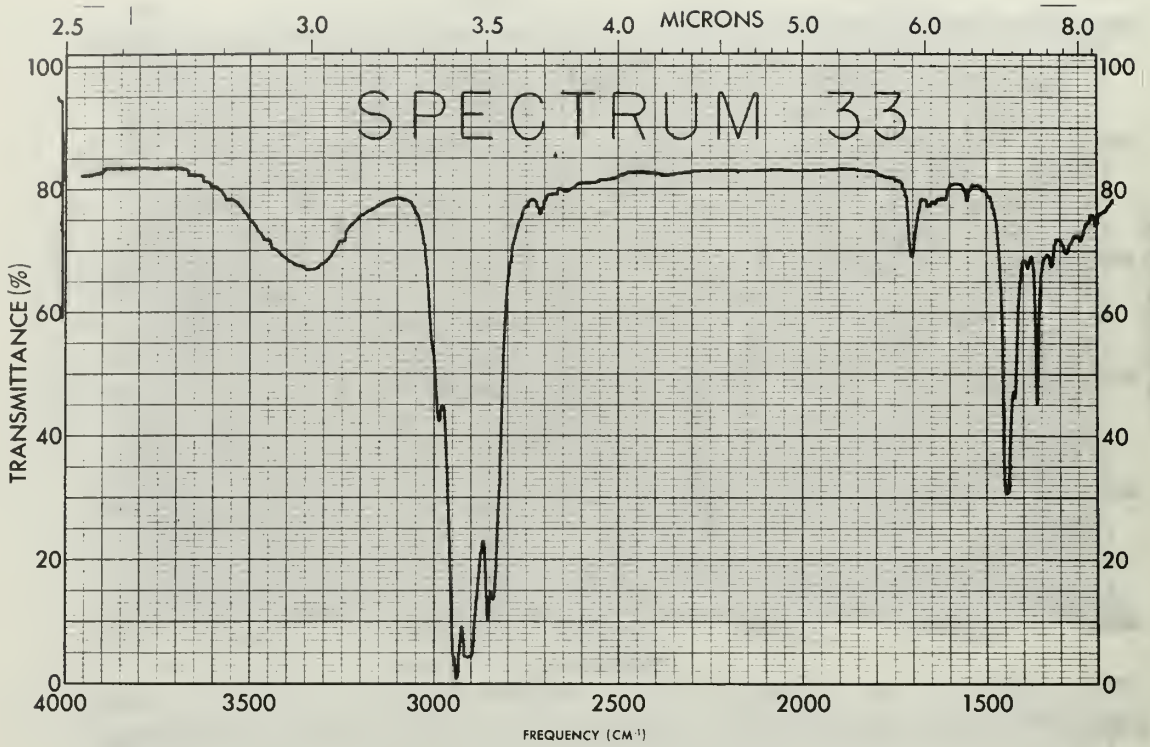

SPECTRUM 28
7.5
8.0
9.0
10.0
MICRONS
15.0
20.0
25.0
100
80
60
40
20
0
TRANSMITTANCE (%)
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (CM⁻¹)

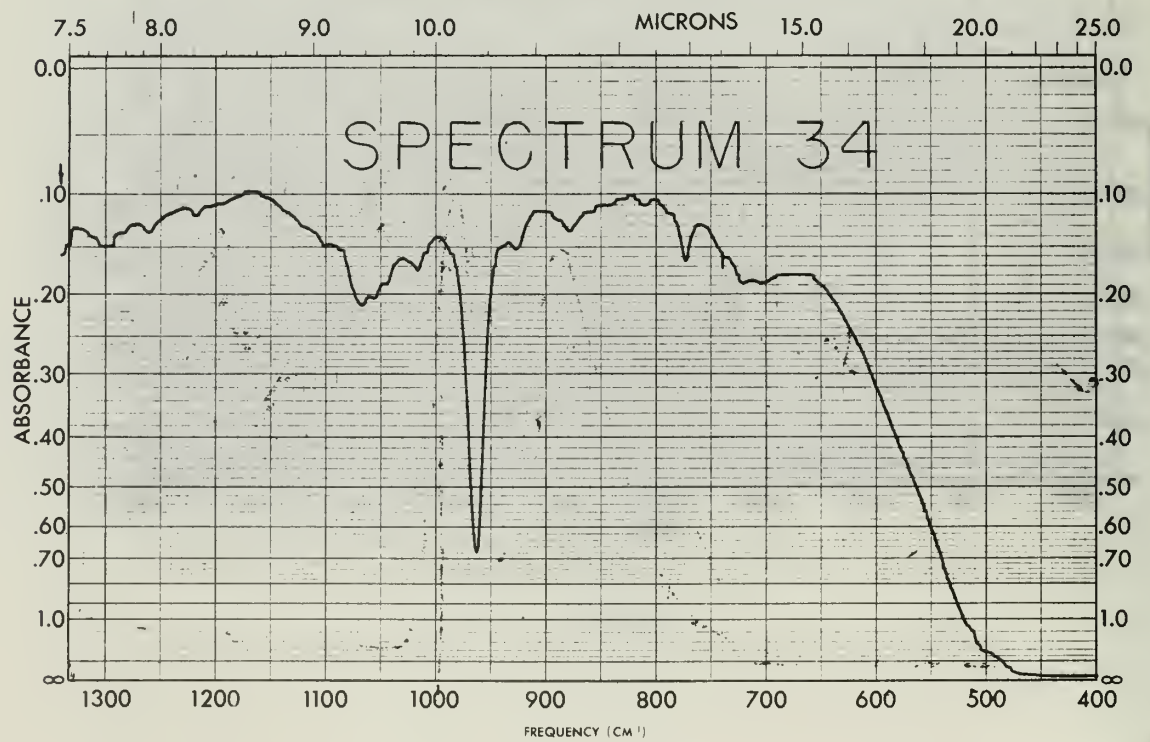

SPECTRUM 29
2.5
3.0
3.5
4.0
MICRONS
5.0
6.0
8.0
100
80
60
40
20
0
TRANSMITTANCE (%)
4000
3500
3000
2500
2000
1500
FREQUENCY (CM⁻¹)


SPECTRUM 30
7.5
8.0
9.0
10.0
MICRONS
15.0
20.0
25.0
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
∞
ABSORBANCE
1300
1200
1100
1000
900
800
700
600
500
400


SPECTRUM 31
MICRONS
2.5
3.0
3.5
4.0
5.0
6.0
8.0
TRANSMITTANCE (%)
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
FREQUENCY (CM⁻¹)


SPECTRUM 32
MICRONS
7.5
8.0
9.0
10.0
15.0
20.0
25.0
ABSORBANCE
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
∞
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (CM⁻¹)

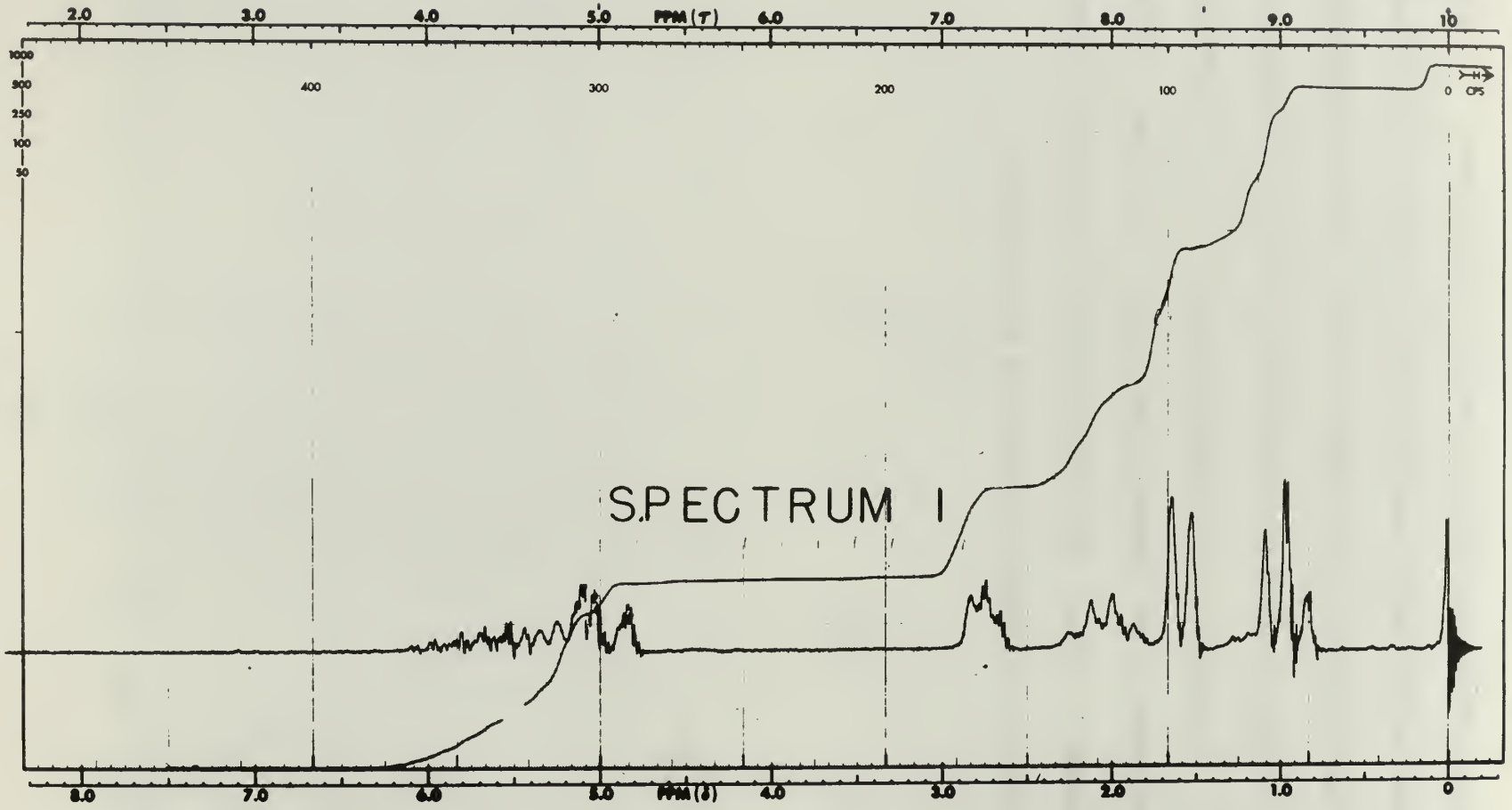

SPECTRUM 33
MICRONS
2.5
3.0
3.5
4.0
5.0
6.0
8.0
TRANSMITTANCE (%)
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
FREQUENCY (CM⁻¹)

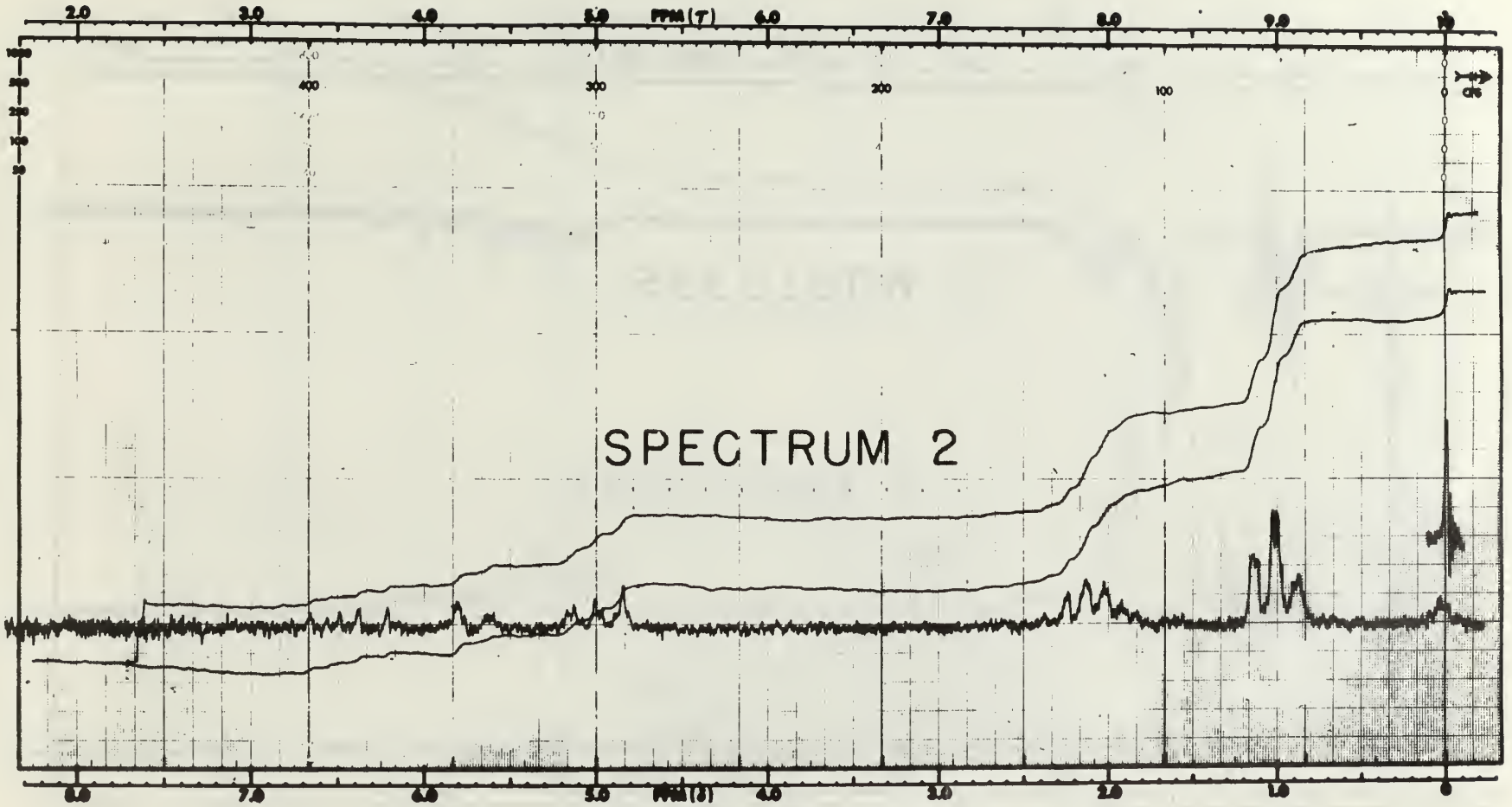

SPECTRUM 34
MICRONS
7.5
8.0
9.0
10.0
15.0
20.0
25.0
ABSORBANCE
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
∞
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (CM⁻¹)

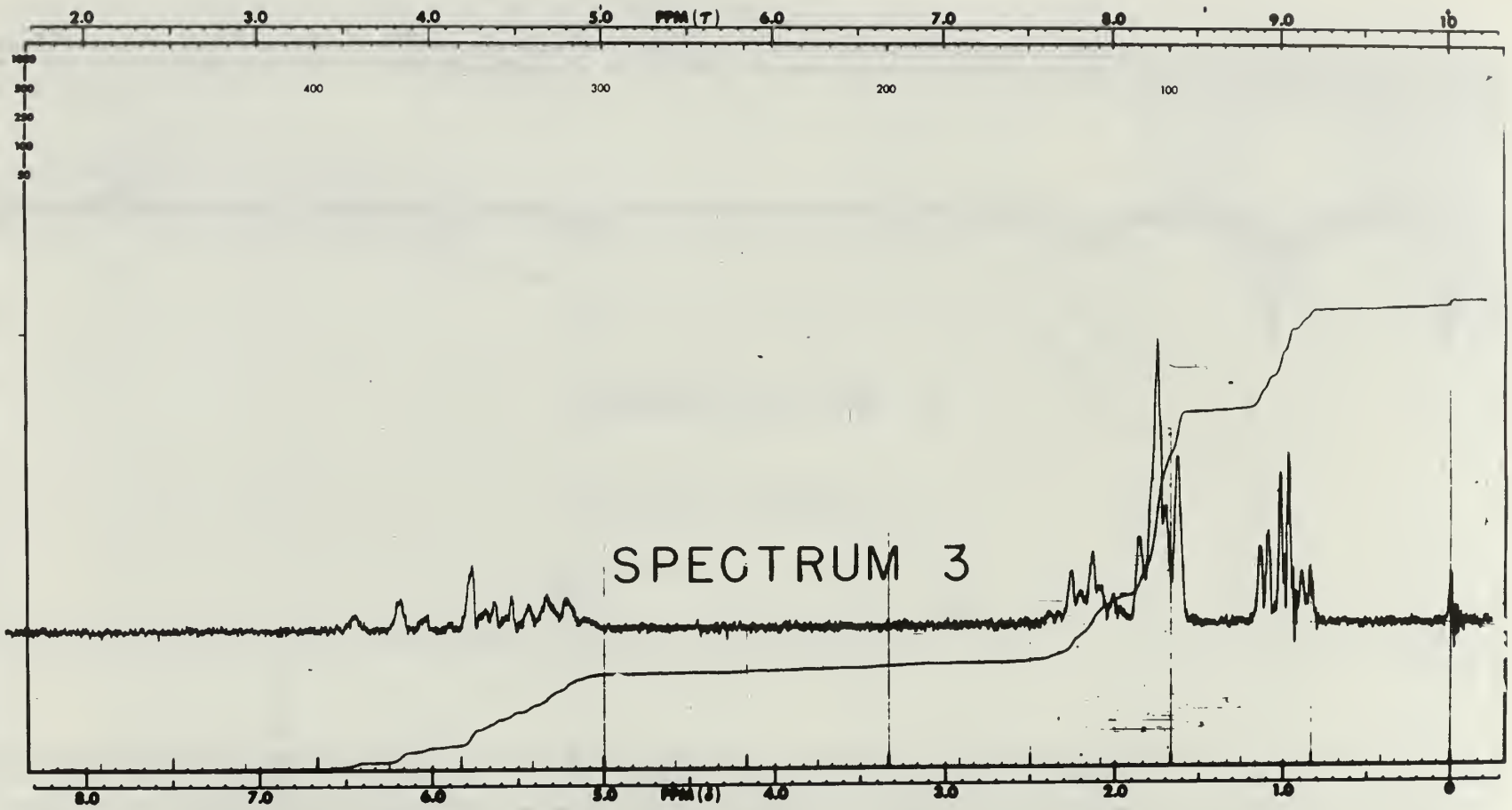
APPENDIX II

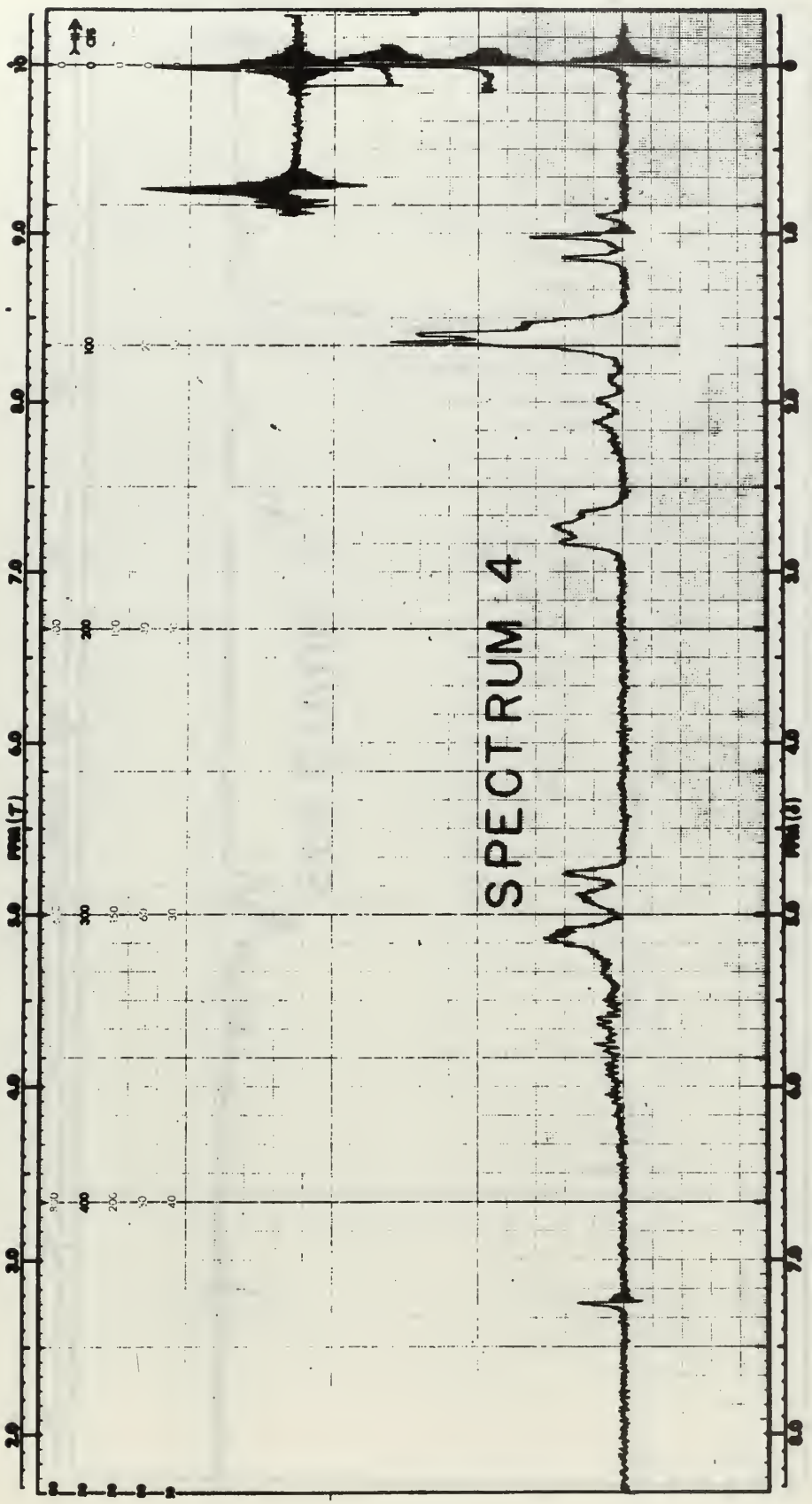
The proton magnetic resonance spectra found in this Appendix were recorded on a Varian Model A-60 Spectrometer. The spectra were recorded using tetramethylsilane as the internal standard. For analysis liquids were in carbon tetrachloride or deuterochloroform. The table of contents for this Appendix appears in Appendix I.

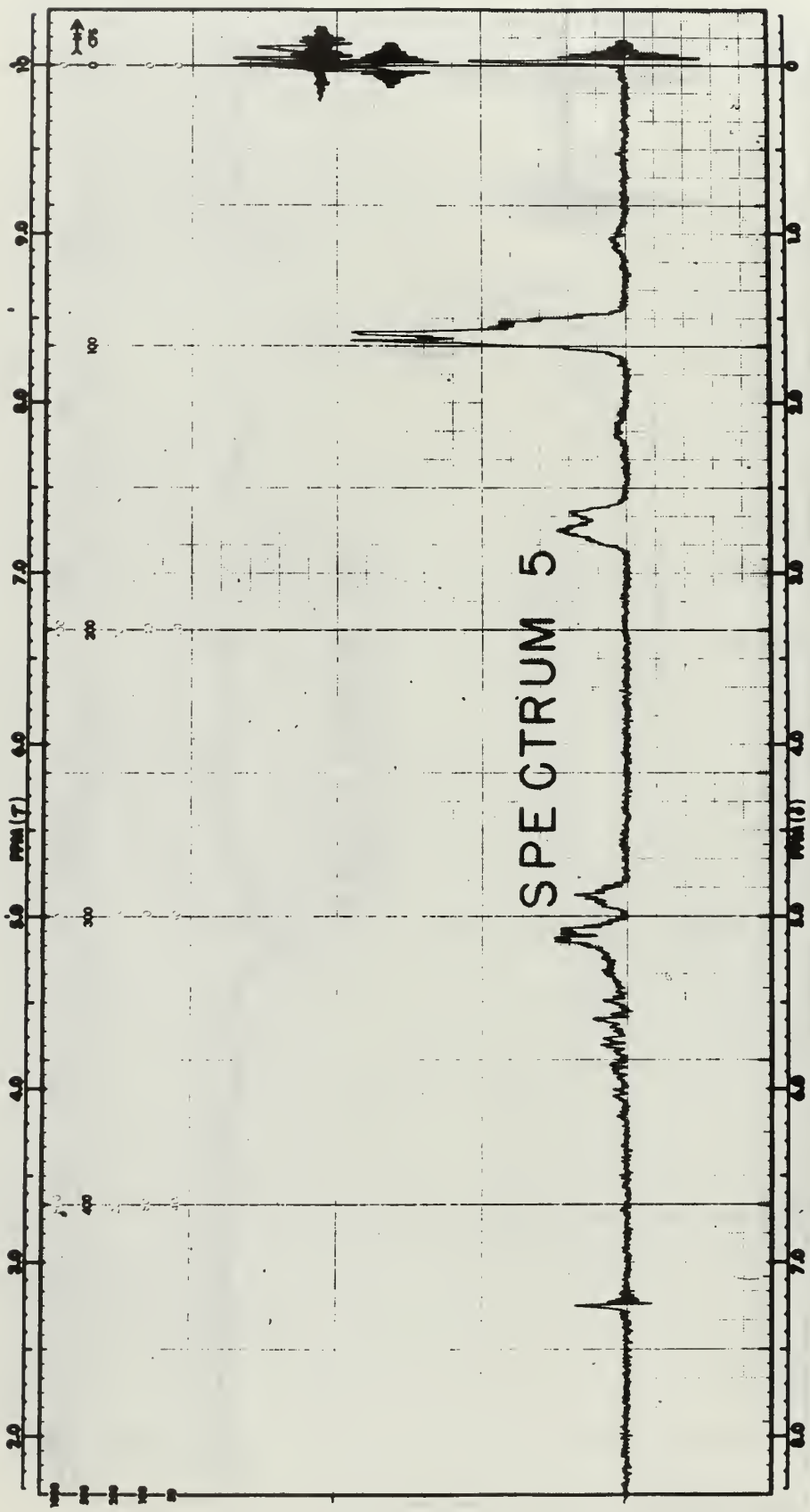
The spectra in this Appendix were recorded at the Michelson Laboratory, Naval Ordnance Test Station, China Lake, California, by Donald W. Moore. His vital assistance in analysing the products made in this research is gratefully acknowledged.

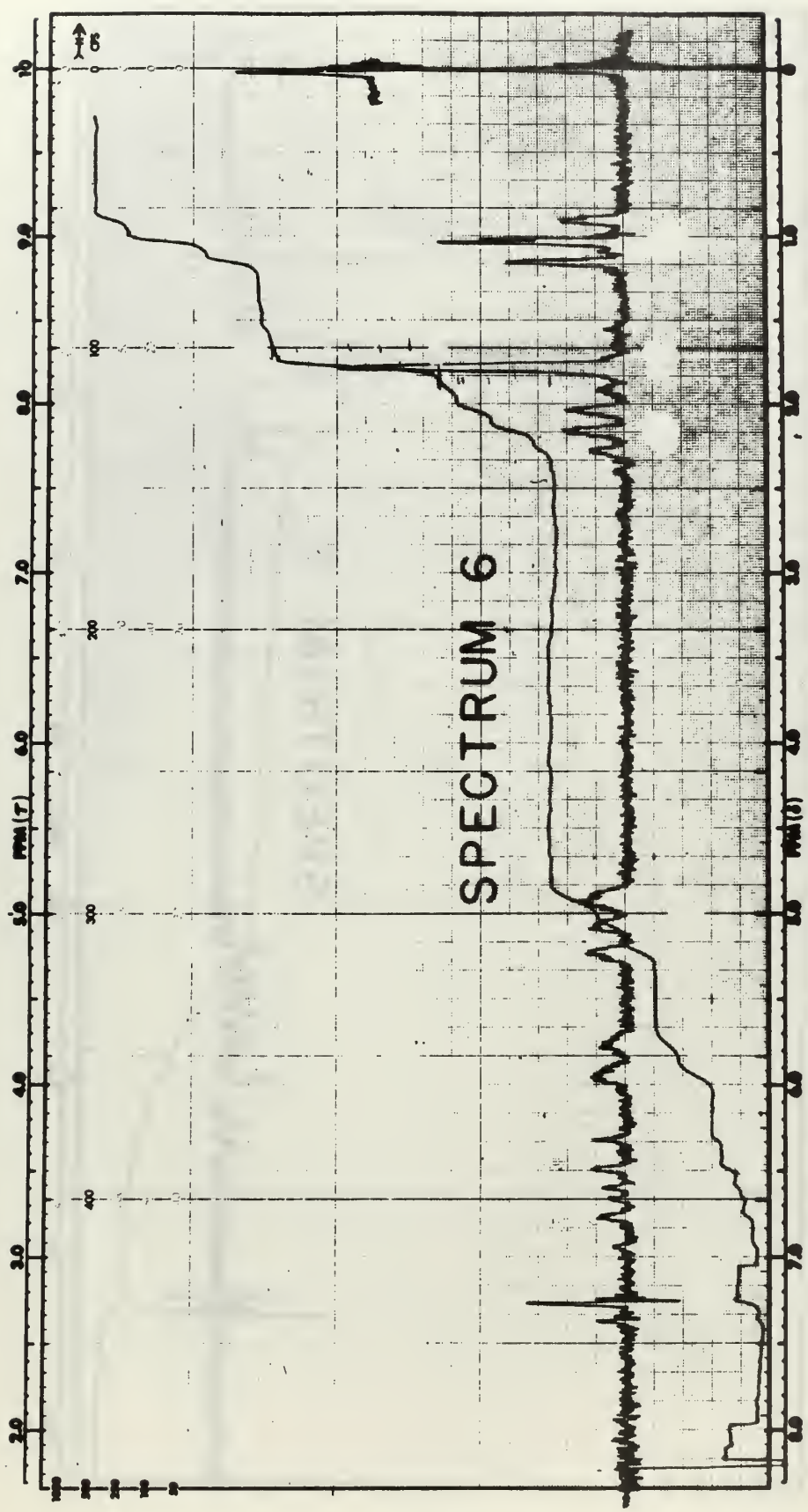

2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
1000
500
250
100
50
400
300
200
100
0 CPS
SPECTRUM I
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

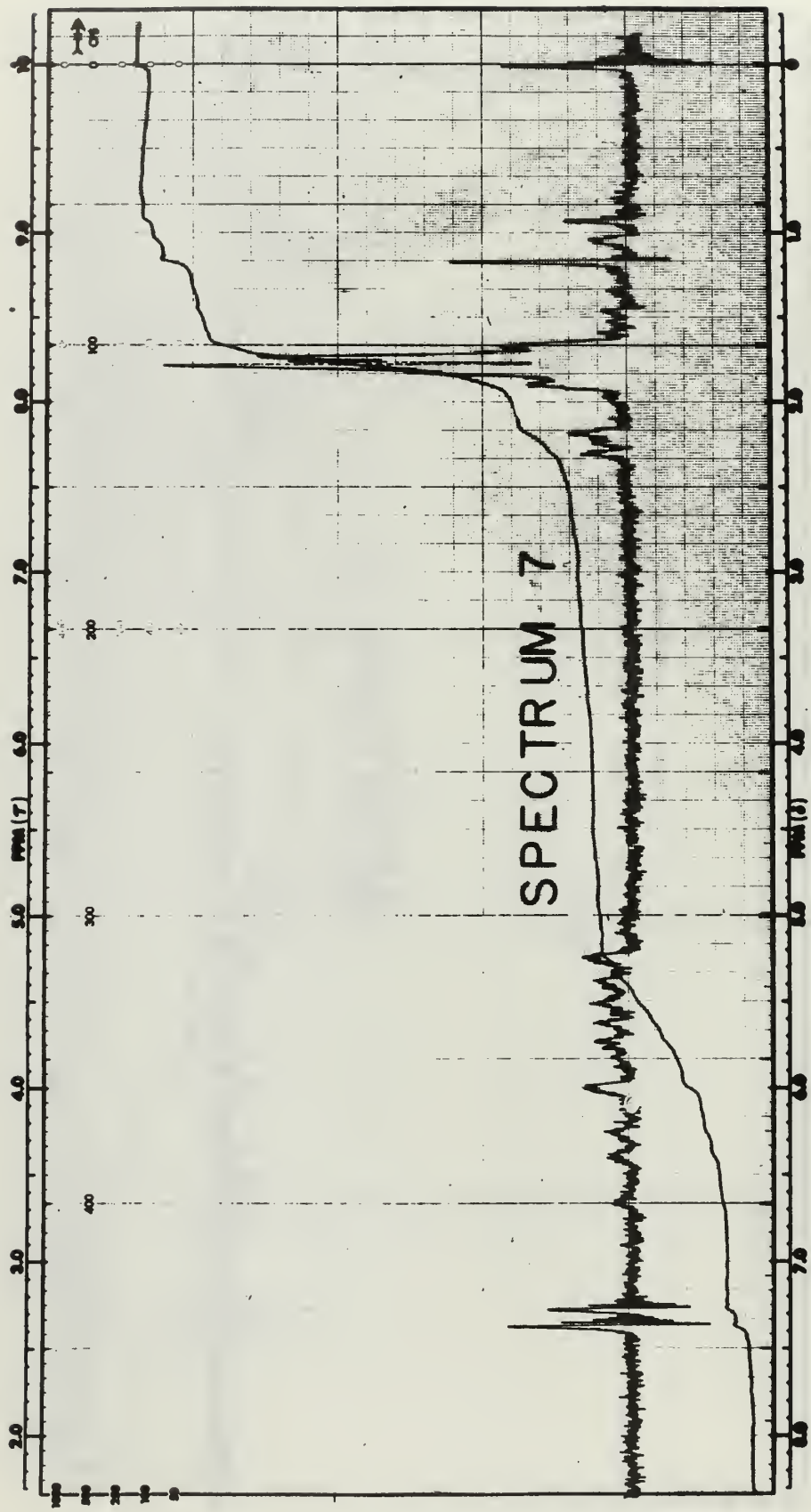

SPECTRUM 2

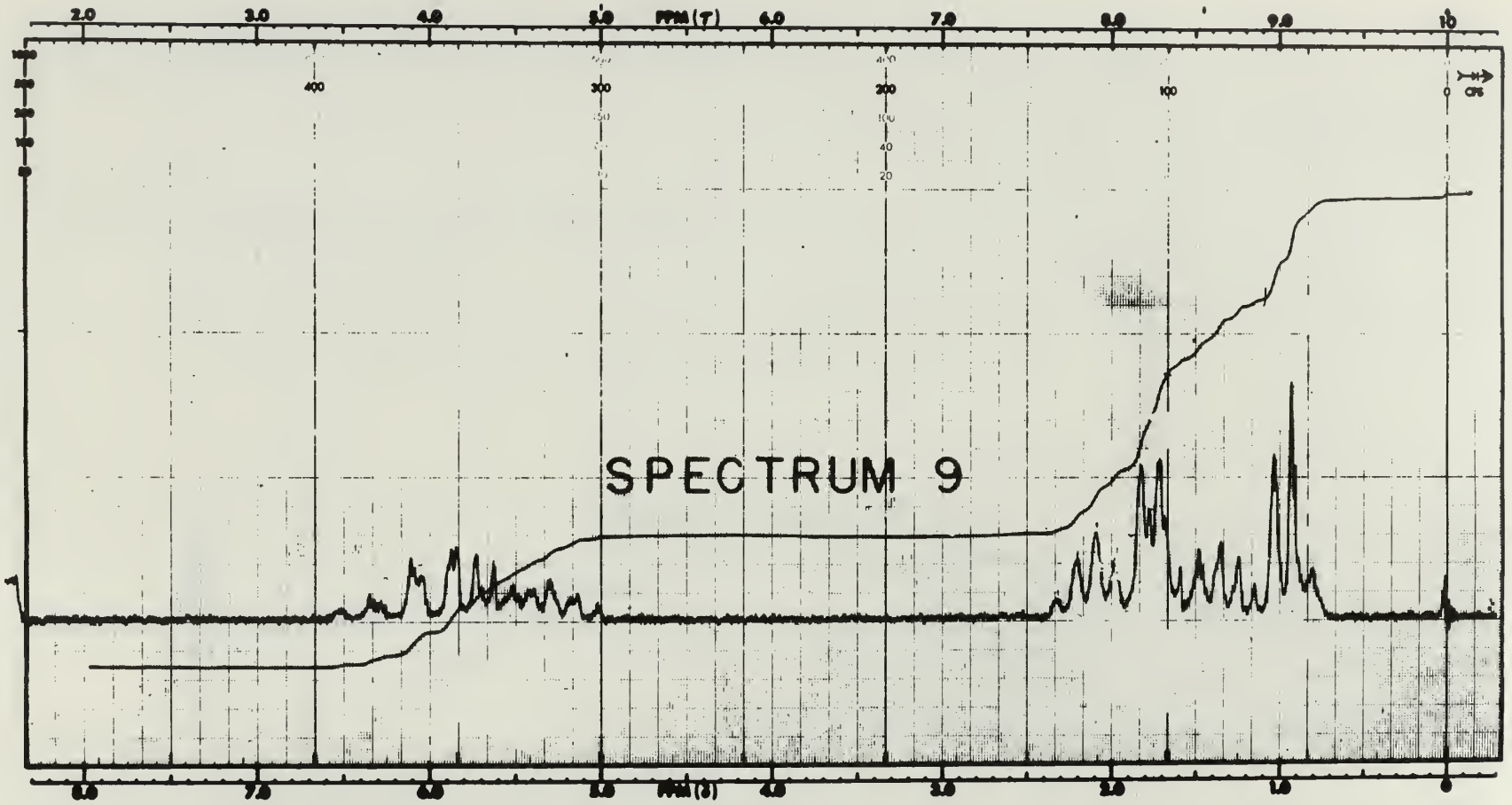

2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
400
300
200
100
SPECTRUM 3
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

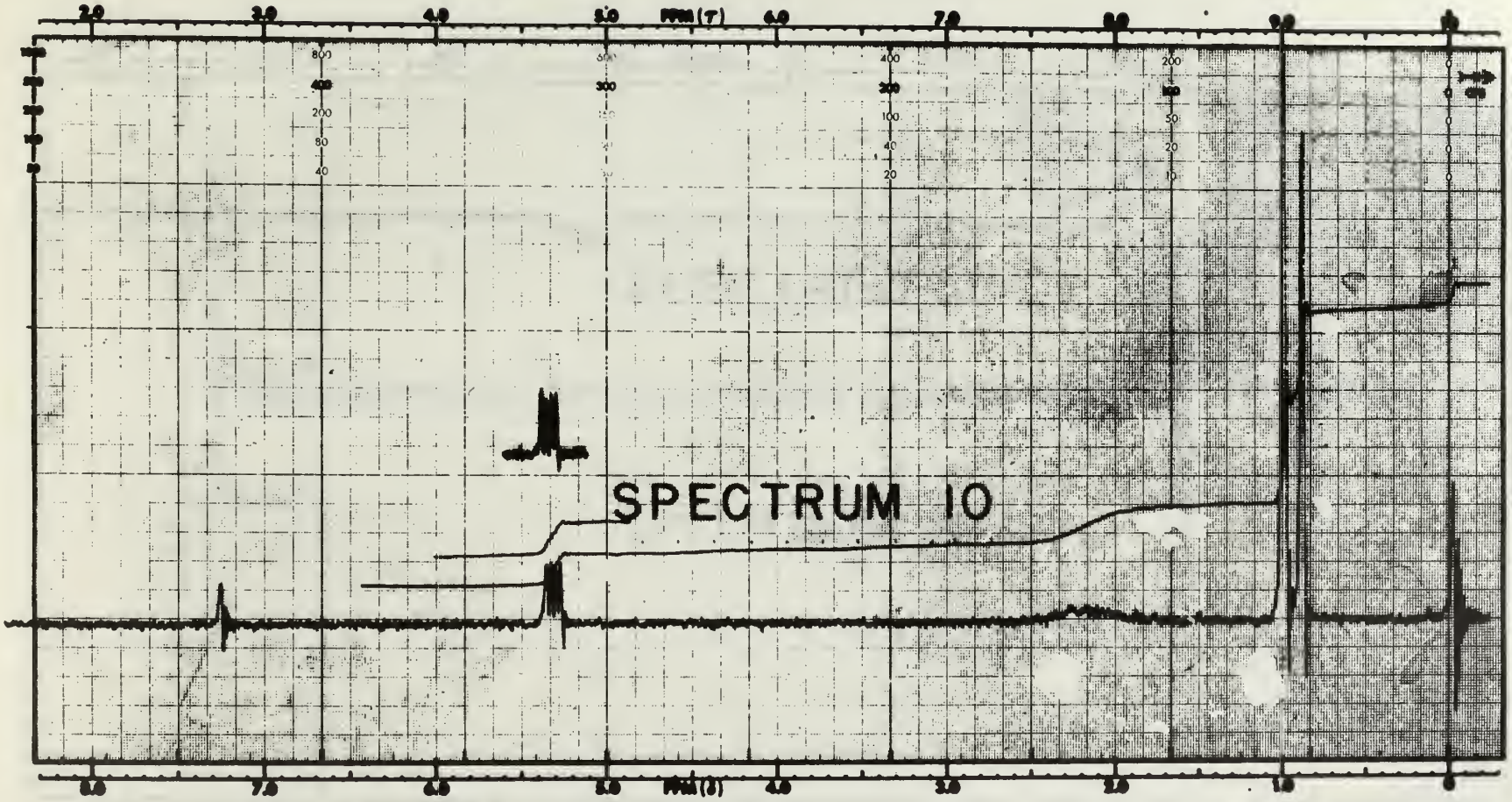

SPECTRUM 4

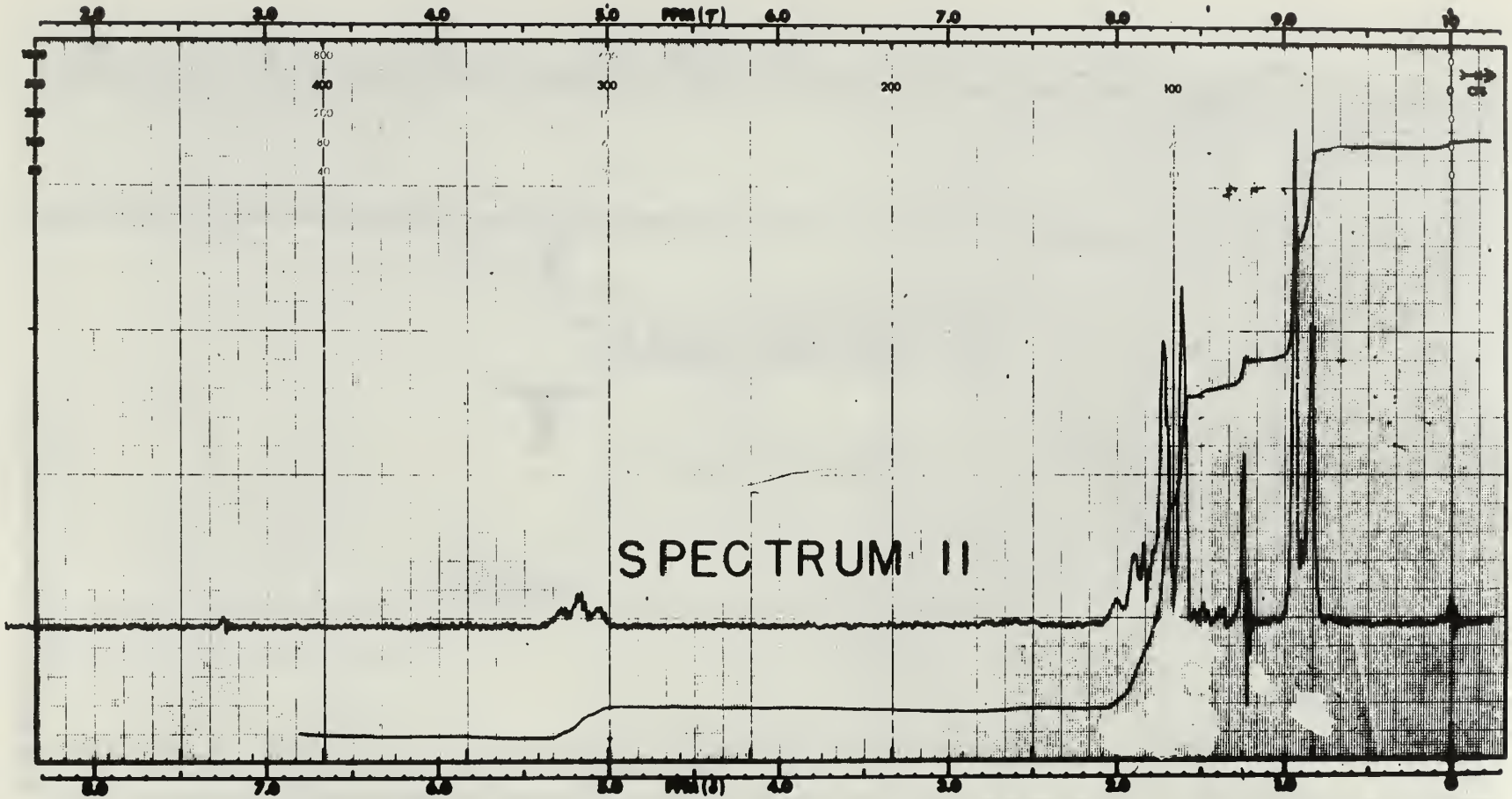

SPECTRUM 5

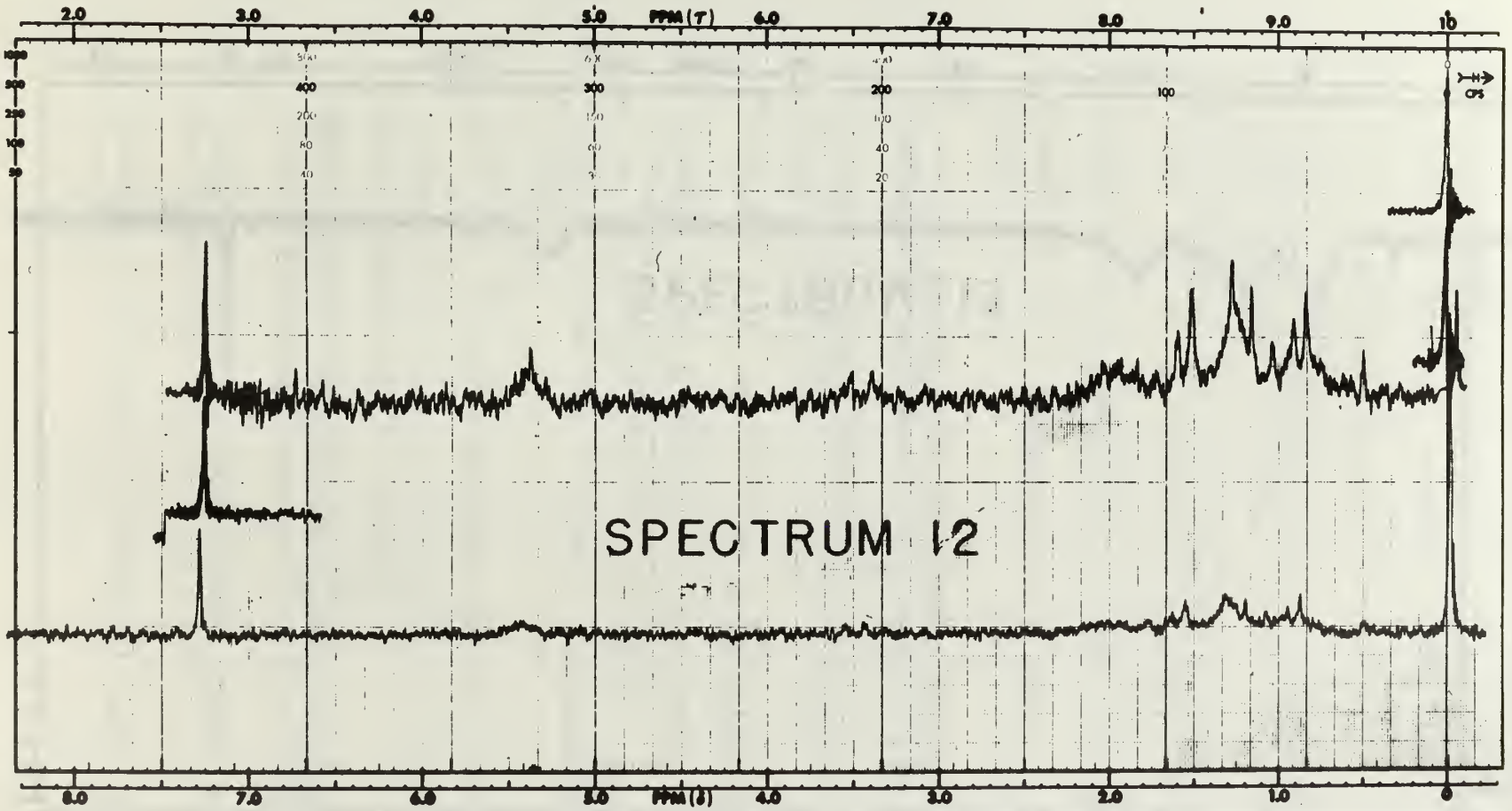

SPECTRUM 6
PPM(F)
PPM(F)

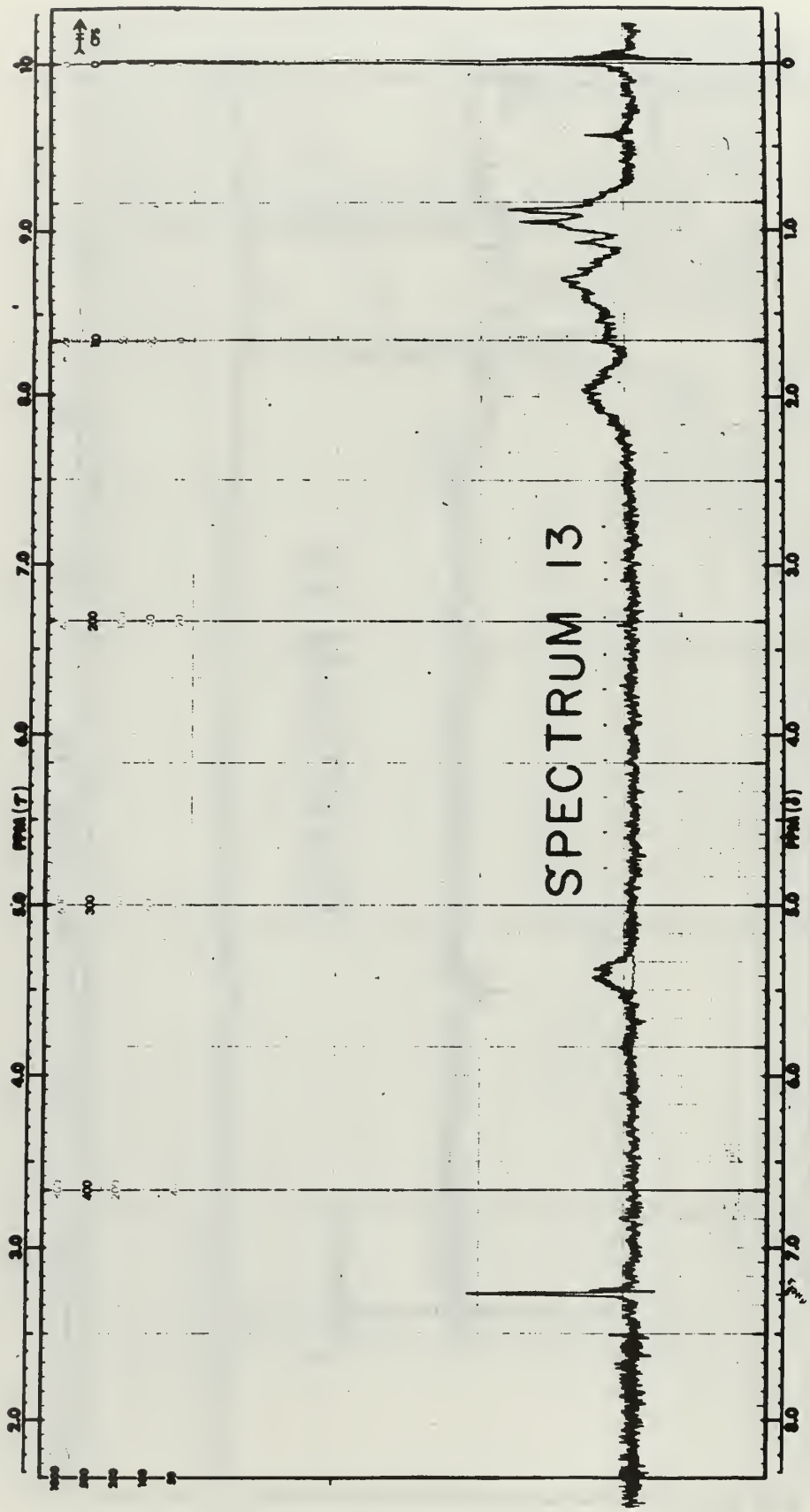

SPECTRUM 7
PPM(T)
PPM(T)


SPECTRUM 9


SPECTRUM 10


SPECTRUM II


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
PPM (δ)
SPECTRUM 12


SPECTRUM 13
PPM(F1)
PPM(F2)

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13. ABSTRACT

A series of alkadienes was prepared by the dehydration of unsaturated C_7 and C_8 alcohols. The dienes were separated by G.P.C. techniques and identified by their NMR and IR spectra. The UV data of the conjugated dienes were also recorded.

The dehydration of 4-ethyl-1-hexen-4-ol gave three dienes, 4-ethyl-1, 3-hexadiene, 4-ethyl-1,4-hexadiene and 3-ethyl-2,4-hexadiene. The dehydration of 4-methyl-1-hexen-4-ol gave four dienes, 4-methyl-1,4-hexadiene, 2-ethyl-1,4-pentadiene, 4-methyl-1,3-hexadiene and 3-methyl-2,4-hexadiene. The dehydration of 4-octen-2-ol gave 1,3-octadiene and 2,4-octadiene in about equal amounts.

The sodium-ammonia reduction products of 2,5-dimethyl-2,4-hexadiene, 1,3-octadiene, and 2,4-octadiene were determined. The reduction of 2,5-dimethyl-2,4-hexadiene gave both the symmetrical and unsymmetrical olefin as reduction products. One reduction of 1,3-octadiene gave 2-octene. The other reductions of 1,3-octadiene and 2,4-octadiene gave mixtures of olefins as their monomeric products.

14. KEY WORDS	LINK A		LINK B		LINK C	
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BIRCH REDUCTION						

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